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The NBS Standard Hygrometer



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A gravimetric hygrometer is described that serves as the NBS standard instrument for the measurement of the moisture content of gases on an absolute basis in terms of mixing ratio (mass water vapor/unit mass of dry gas). The National Bureau of Standards and other laboratory reference and working instruments are compared and calibrated with this instrument. The measuring operation involves the absorption of the water vapor from a water vapor-gas mixture by a solid desiccant and the determination of the mass of this water vapor by precision weighing; it also involves the determination of the volume of the associated gas of known density by counting the fillings of two calibrated stainless steel cylinders. An automatic system permits the sampling of the test gas at any desired flow rate up to 2 liters per minute (STP) and for any desired number of fillings. The instrument provides a value of the mixing ratio averaged over the time interval of a test.

The construction and operation of the instrument is described. Discussions of the tests and calibrations of component parts, and of the sources of errors also are included. An analysis of the random and systematic errors effecting the overall accuracy in the determination of mixing ratio shows that if 0.60 g of water vapor is collected from moist air, then the estimated maximum uncertainty expected for mixing ratios between 27 mg/g and 0.19 mg/g is 12.7 parts in 10^4 .

1. Introduction

The measurement of the water-vapor content of gases has been assuming an ever increasing importance in many disciplines of our modern science and technology. The expanding number and frequency of humidity measurements now being made has brought to the fore a need for increased accuracy in measurement, and with it, a need for fundamental standards. To fulfill this need, the National Bureau of Standards has developed an improved hygrometer, based on the gravimetric method, to be used as the NBS standard hygrometer for comparison with, and calibration of, lower order standard instruments.

The gravimetric method is well known in the arts of hygrometry [1-12]¹, chemical analysis [13], and vapor pressure measurement [14-27]. It was chosen as the standard because it yields a measure of water vapor content in absolute units of mass of water vapor per unit mass of associated dry gas, that is, mixing ratio, which measurement may be made with great inherent precision and accuracy.

Through the use of selected physical equations, mixing ratio may be converted to other units of humidity, such as vapor pressure, relative humidity, and saturation deficit.

Mixing ratio is defined by the equation

$$r = M/(V\rho)_{t,B} \quad (1.1)$$

where

r = mixing ratio, mass of water vapor per unit mass of dry gas, g/g

M = mass of water vapor, g

V = volume of the dry gas associated with the mass of water vapor, cm^3 at temperature t and pressure B

ρ = density of the dry gas associated with the mass of water vapor, g/cm^3 at the temperature t and pressure B .

The subscripts t and B merely emphasize the pressure-temperature dependence of the density and volume, and will not appear in subsequent sections.

The experimental conditions under which the gravimetric hygrometer operates fulfill the requirements of this equation for yielding mixing ratio. The water vapor admixed with a gas is absorbed by a desiccant and precisely weighed. The pressure and temperature of a known volume of this dry gas are measured, from which values the gas density may be computed. The product $V\rho$ then yields the mass of the dry gas.

Humidity measurements are now being made for scientific and industrial purposes with accuracies approaching 1 percent. In order to calibrate instruments to this accuracy, it was considered desirable that the NBS standard hygrometer have an accuracy of at least 0.1 percent. To achieve this accuracy, a goal was set of measuring each of

¹Figures in brackets indicate the literature references on page 32.

the parameters that contribute to the mixing ratio with an accuracy of 1/10,000.

The gravimetric hygrometer is a device which provides an average value of the moisture content in the test gas; however, the test gas must be sampled for periods of time long enough to insure that the mass of water absorbed by the desiccant may be weighed with requisite accuracy, yet it must not be sampled so long that factors such as system leaks begin to contribute significant error. The time of a run varies roughly from 5 minutes to 30 hours with the present apparatus, depending on the humidity of

the test gas and the sampling flow rate. In comparing another instrument with the gravimetric hygrometer at a given test gas moisture content, it may be necessary to take repeated readings on the instrument undergoing calibration in order to obtain a corresponding average value for its indication. A humidity generator [28, 29] provides the test gas of constant moisture content for calibration purposes.

The gravimetric hygrometer has been used to check and calibrate this generator [29], and has also been used for the calibration of the NBS pneumatic bridge hygrometer [30].

2. Description

2.1. General Process Description

To prepare the gravimetric hygrometer for use, the components of the test gas flow path must be purged to insure that there is no extraneous moisture to be picked up when the preweighed, desiccant filled vessels, which will remove the moisture from the test gas, are inserted. For this operation, Pyrex bridges or jumpers are inserted to complete those parts of the flow path occupied by the desiccant vessels during the test. A gas, usually tank air, is passed through a purging gas drying system, which consists of a second set of (unweighed) desiccant filled vessels, and then on through the test gas flow path.

Upon completion of the purging operation, the purging gas drying system is isolated from the remainder of the system by means of a valve, the bridges are removed, and the preweighed, desiccant filled vessels which comprise the main (or test gas) drying train are inserted in their places.

The test gas provided by the humidity generator is now sampled simultaneously by an instrument under calibration and by the gravimetric hygrometer.

After entering the gravimetric hygrometer, the test gas passes first through the desiccant filled vessels, where the moisture is removed.

The dried gas then passes into one of two chambers whose volumes have been calibrated. Once in the chamber, the gas is allowed to come to equilibrium, at which time the temperature and pressure are measured. As stated previously, knowledge of the temperature, pressure, and volume of the gas permits calculation of its mass. After the temperature and pressure have been measured, the gas is evacuated from the chamber by the vacuum pump.

During the time necessary to attain equilibrium in, perform measurements on, and evacuate one chamber, the other chamber fills. The timing is such that when one chamber has been evacuated, the other has finished filling, and the roles of the two are then reversed. The valve sequencing is automatically controlled by the pressure switch.

A test is terminated when enough test gas has been drawn through the system to insure that the

water vapor removed by the desiccant may be weighed with sufficient accuracy. This usually requires multiple fillings of the chambers.

The weight of the desiccant vessels before and after the test allows computation of the water mass, while the associated dry gas mass is the sum of the masses that passed into the chambers.

These two quantities and eq (1.1) allow calculation of the mixing ratio, which is in fact the average mixing ratio for the test period.

The readings of the instrument which has been under calibration are averaged, and by proper conversion of units, that average and the value obtained from the gravimetric hygrometer can be compared.

2.2. Components

The essential components of the apparatus are shown in block diagram in figure 1 and schematically in figure 2. The apparatus comprises a purging gas drying train, a main drying train for the test gas, a flow controller, a gas volume measuring system which is housed in a thermostatted oil bath, a five-level pressure switch, a vacuum pump, temperature and pressure measuring instruments, and suitable valves and controls. An auxiliary refrigerated bath is used to control the temperature of the oil bath. The electric and electronic controls, together with the drying trains, flowmeter, and flow controller, are assembled on a relay rack.

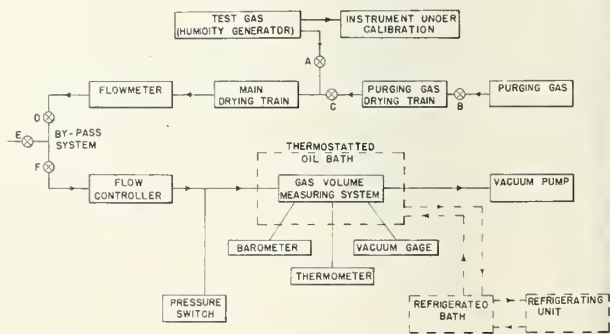


FIGURE 1. Block diagram of the gravimetric hygrometer.

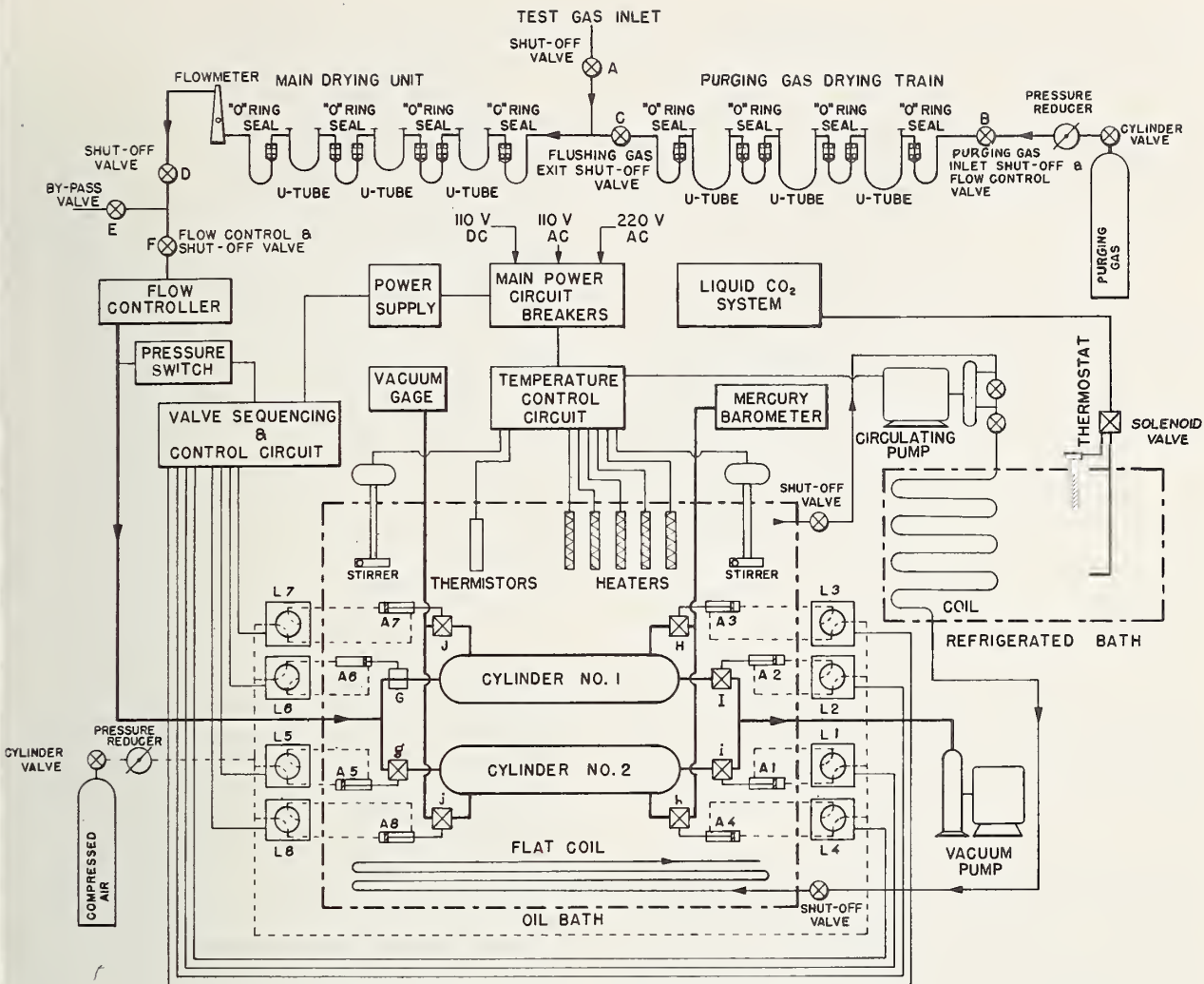


FIGURE 2. Schematic diagram of the gravimetric hygrometer.

Type 316 stainless steel is used for all interconnecting tubing, and, where possible, the valves are of type 316 stainless steel with Teflon components. These materials are used to minimize the effects of water sorption and reactions with various matter.

a. Main Drying Train

The main drying train consists of three interchangeable absorption U-tubes (the desiccant vessels mentioned in sec. 2.1) and six "O" ring seals for pneumatically connecting the U-tubes to one another and to other parts of the apparatus. Its function is to absorb the water vapor completely from the test gas. The first U-tube, which is filled with anhydrous $\text{Mg}(\text{ClO}_4)_2$, and backed with a plug of P_2O_5 absorbs all, or nearly all, of the water [31, 32]. The second and third tubes are filled with anhydrous P_2O_5 [33]. If the desiccant in the first U-tube is near exhaustion or if the airflow is too rapid, some moisture may remain in the effluent gas. The second tube removes the trace amount that is still

left. The third tube serves as a guard. If water vapor is inadvertently present downstream of the main drying train, the third tube prevents it from diffusing back to the second tube.

Each U-tube, fabricated from Pyrex glass, has the shape and dimensions of the smaller unit shown in figure 3. The side arms are designed to fit into the "O" ring seals. The empty tube weighs about 70 g. and, when filled with desiccant, about 80 g.

Stainless steel connectors hold and interconnect the U-tubes to one another and to the rest of the apparatus so that a path is available for gas flow. These connectors are fabricated from 5/16-in. o.d. type 316 stainless steel tubing. Coupling nuts, with "O" ring seals, are attached to the tubing. The U-tube side arms are inserted into the coupling nuts and sealed into the system through the compression of neoprene "O" rings. Teflon "O" rings seal the coupling nuts to the stainless steel tubing. Pyrex bridges are used, on occasion, in place of the U-tubes to allow gas to flow through the system or to

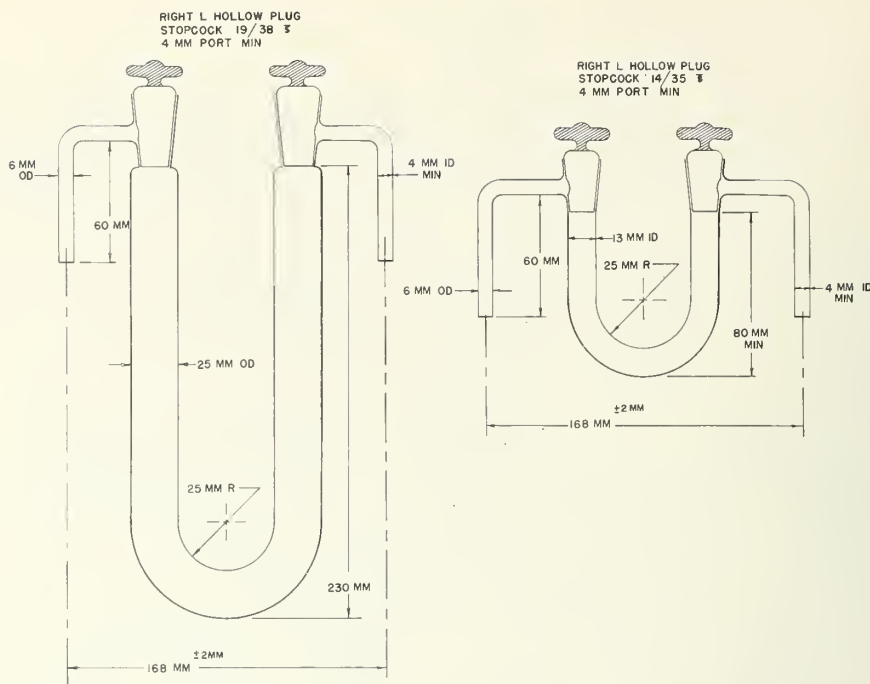


FIGURE 3. Drying tubes.—Flushing gas drying train U-tube (left); main drying train U-tube (right).

protect the drying train components from direct exposure to atmospheric air. These bridges are made to fit into the "O" ring seal connectors.

b. Flow System

A dry gas is used to purge and dry various parts of the apparatus prior to a test. This purging gas is supplied from a compressed gas cylinder, through a pressure reducer, and is dried by a separate drying train that is similar in all respects to the main drying train, except that large U-tubes (fig. 3) are used. The rate of flow is adjusted by the inlet flow control and shutoff valve *B* (refer to figs. 1 and 2), which is a brass globe metering valve, 1/4 in. size, with Teflon seat. The main system can be pneumatically isolated from the flushing gas drying train by closing valve *C*.

The test gas enters the apparatus through a 1/4-in. compression fitting upstream of the shutoff valve, *A*. The downstream port of the valve is connected to a connector on the main drying train and to the downstream port of the flushing gas exit shutoff valve, *C*. Both valves are stainless steel (type 316) packless high-vacuum valves, with Teflon diaphragms, and 3/16 in. diameter ports.

A taper-tube and float type of flowmeter, with maximum flow rate of 1.9 STP liters of air per minute is located immediately downstream of the main drying train. This instrument serves primarily to give visual indication of the nominal flow rate.

A bypass system is located downstream of the flowmeter. Its purpose is (a) to permit either the test gas or the flushing gas to be exhausted directly to the atmosphere, (b) to isolate or shut off the main

drying train from the rest of the apparatus, and (c) to permit room air, or any other gas, to be drawn directly into the gas volume measuring system without going through the main drying train. The bypass system comprises three valves, *D*, *E*, and *F*, arranged as shown in figure 2. Valves *D* and *E* are stainless steel packless shutoff valves with Teflon diaphragms identical to valves *A* and *C*. Valve *F* is a shutoff and control valve identical to valve *B*.

A mercury Cartesian manostat, together with valve *F*, may be used to maintain any constant flow in the range 0 to 2 liters per minute (lpm).

c. Gas Volume Measuring System

A gas volume measuring system meters the volume of dry gas which has passed through the main drying train. It consists of the following units: two metal cylinders (the calibrated chambers mentioned in sec. 2.1); a vacuum pump for evacuating the cylinders; a vacuum gage for measuring the vacuum pressures within the cylinders; a precision barometer for measuring near-atmospheric pressures within the cylinders; suitable valves for connecting either cylinder to the main drying train, the vacuum pump, the vacuum gage, and the barometer; a pressure switch for sensing pressures within, and controlling the open-closed position of the valves of the cylinders; and auxiliary control circuits. The vacuum pump evacuates each cylinder in turn. By proper sequencing of the open-closed position of the valves, gas is drawn through the main drying train into a cylinder, until the pressure within the cylinder reaches a predetermined value. The gas volume is then the calibrated capacity of the cylinder.

der at the final temperature and pressure of the gas. While gas is entering one cylinder, the other cylinder is evacuated, producing in this way a continuous flow through the main drying train.

Each cylinder is fabricated from type 316 stainless steel and has a nominal volumetric capacity of 30 liters. Each cylinder has a port into which a four junction copper-constantan thermopile is inserted to measure the gas temperature therein. The emf output of each thermopile is measured with a precision laboratory potentiometer; the unbalance of the latter is detected by a d-c breaker amplifier and a 1-milliamperere range pen and ink recorder. The potentiometer may be connected to either of the thermopiles through a rotary double-pole thermocouple switch. A compression fitting provides a seal for the thermopile and also allows the thermopile to be removed for calibration or replacement. Each cylinder has an inlet port through which the gas enters, an exit port through which the cylinder is evacuated, a barometer port, and a vacuum gage port. These ports are connected, through "O" ring flanged couplings, to remotely controlled valves, and then to the appropriate components of the apparatus.

All valves communicating with the cylinders are high-vacuum, ball-type, shutoff valves. Each valve is separately opened or closed by an air-operated piston which, in turn, is actuated by a solenoid valve. The arrangement is shown schematically in figure 2. The air-inlet valves, *G* and *g*, the barometer valves *H* and *h*, and the vacuum gage valves, *J* and *j*, are 1/4-in. pipe size, with unrestricted through passages in their open positions. The vacuum exhaust valves, *I* and *i*, are 1-1/2-in. pipe size, with unrestricted through passages in their open positions. All pipe, tubing, and fittings are fabricated from type 316 stainless steel.

d. Pressure Switch

As shown in figure 2, a pressure switch is located so that it may be placed in pneumatic connection with either cylinder through the inlet valves, thus sensing the pressure in the cylinder. The switch is in the form of a fixed cistern mercury barometer, with light sources, photocells, and a control circuit so arranged that absolute pressures of about 700, 690, 410, 400, and 50 mm Hg are detected. As the mercury column rises and falls in response to the pressure in one or the other cylinder, the photocell circuits are sequentially interrupted, sending pulses to appropriate relays which in turn operate the required valves.

This provides not only for the continuous and automatic drawing of the test gas through the cylinders, but also for periodic sensing by a barometer of the pressure within the cylinders.

The mercury barometer, with vernier slide mechanism, sighting tube and illuminating lamp removed, is mounted in an enclosed metal housing. Parallel to the barometer is a guide rod on which are mounted five aluminum forks so arranged that the

barometer tube passes between the two tines of each fork. One tine has a 1/4-in. diameter hole in which a selenide photocell is inserted; the other tine is machined to hold a lamp bulb. The light from the lamp passes through a one-mm diameter hole and onto the barometer tube. A plug with a $3/32 \times 0.010$ -in. slot acts as a diaphragm in front of the photocell. The forks are placed on the guide rod so that the photocells will respond at the five designated pressures.

e. Automatic Control Circuit

The main function of the automatic control circuit is to open and close the cylinder valves in such an order that each cylinder alternately is evacuated and then filled with the test gas so as to maintain a continuous flow through the drying train. Consider the filling operation of cylinder no. 2. During the first half of the filling of no. 2, cylinder no. 1 remains sealed and filled with the dried test gas. Enough time is allowed for no. 1 to come to temperature-pressure equilibrium, and these quantities are measured. At this stage of the operation, valve *g* (inlet valve to cylinder no. 2) and valve *H* (barometer valve to cylinder no. 1) are open. When cylinder no. 2 is nominally half full, valve *H* closes. A moment later, valve *I* opens, allowing the evacuation of cylinder no. 1 during the second half of the filling operation of cylinder no. 2. When cylinder no. 2 is almost full, valve *I* closes on cylinder no. 1, which has now been evacuated to a pressure of about 20μ Hg. After a brief pause, valve *g* (inlet valve to cylinder no. 2) closes and simultaneously valve *G* (inlet valve to cylinder no. 1) opens. After another brief pause, valve *h* (barometer valve for cylinder no. 2) opens, and the process continues as above with the cylinders exchanged.

The residual pressure in a cylinder during evacuation may be measured with the vacuum gage by manually opening the appropriate valve *J* or *j*.

The manipulation of the valves associated with the two cylinders is sequenced and controlled by the circuit shown in figure 4. In response to signals from the pressure switch, one or more relays are either energized or deenergized. These relays position the ports of four-way solenoid valves *L1*, *L2*, *L3*, *L4*, *L5*, *L6*, *L7*, and *L8*. The latter apply pressure to air cylinders *A1*, *A2*, *A3*, *A4*, *A5*, *A6*, *A7*, and *A8*, which actuate cylinder valves *G*, *H*, *I*, *J*, *g*, *h*, *i*, and *j*.

The detailed operation of the circuit is given in the appendix.

An electrical counter *M* is used in parallel with each solenoid valve actuating valves *G* and *g*. These counters indicate the number of times these cylinder valves open, and so measure the number of times each cylinder is filled.

f. Temperature Control System

An insulated temperature-controlled oil bath houses the gas volume measuring system. Temperatures in the range of 20° to 35°C may be maintained in the oil bath by means of a thermostating

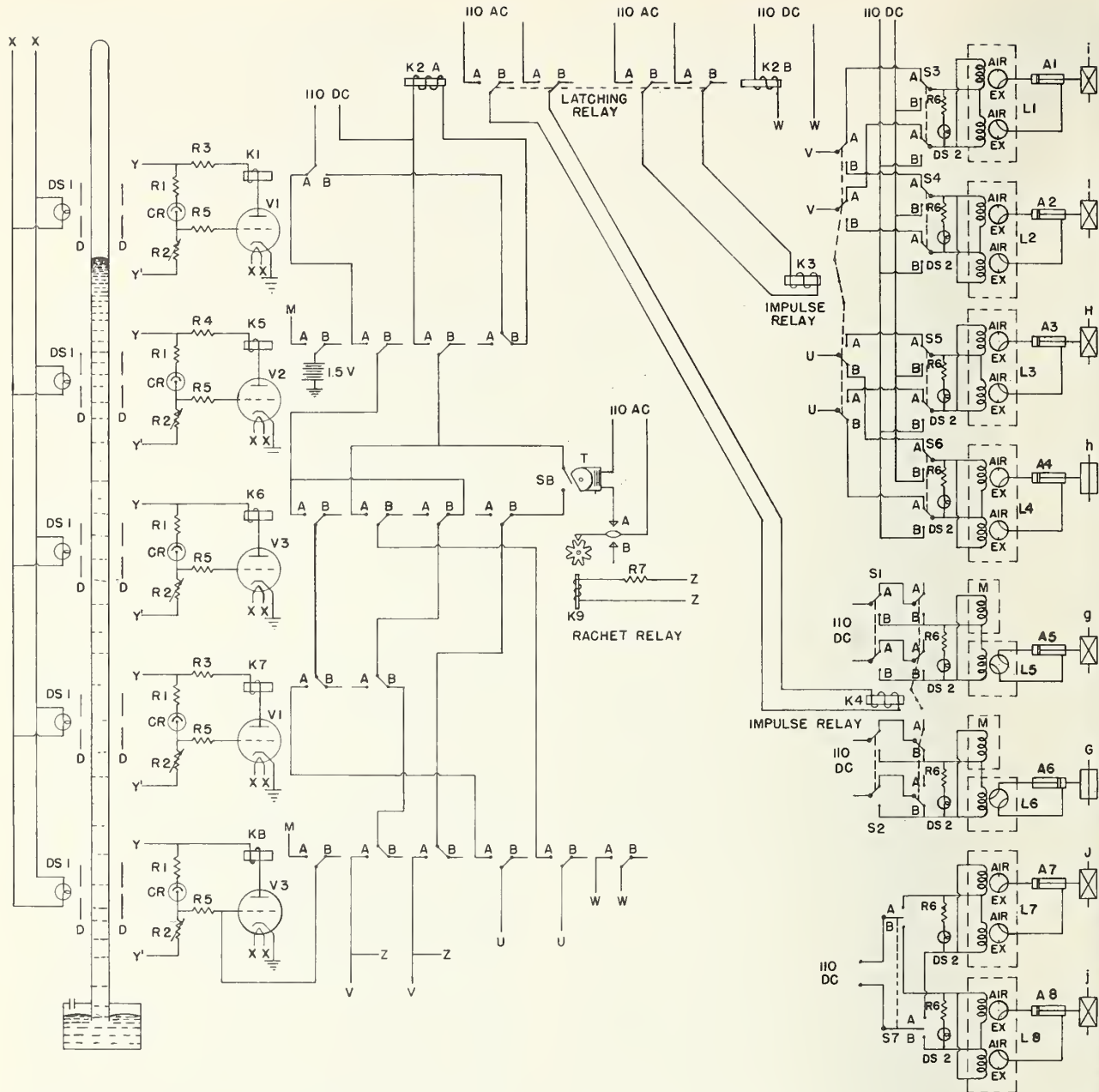


FIGURE 4. Valve sequencing and control circuit. The pressure switch is on the left. Symbols in addition to those explained in the text are: DS1, lamp, 6.3 v; DS2 neon lamp; CR, Cadmium selenide photocell; D, diaphragm for lamp and photocell; XX, 6.3 v a-c; Y, +255 v d-c; Y', -40 v d-c; V₁, V₂, and V₃, 12AT7; R₁, 100 K; R₂, potentiometer, 5M; R₃, 25 K; R₄, 8.2 K; R₅, 180 K; R₆, 100 K; R₇, 300 ohm.

circuit. A Wheatstone bridge, with thermistors and ganged multiple-turn helical potentiometers in the arms, controls the on-off position of one or more heaters while a pump circulates cooled oil from a refrigerated bath into the main oil bath and back. The flow and temperature of the circulated oil are so adjusted that there is a slight tendency for the oil bath to cool. The bridge circuit and control heaters apply the necessary heat to the main oil bath to keep it at the required temperature. Three auxiliary manual heaters are provided for quickly warming the oil bath to the control temperature.

g. Balance Room

All weighings are made in a balance room that is maintained at a constant nominal temperature of 25 °C, and at a low relative humidity and is kept free of dust. A 100-g semi-micro analytical equal-arm balance and a 50-kg high capacity equal-arm balance are located within the balance room. The former rests on a small marble slab on a firm table while the latter rests on a large marble slab which is supported by two steel I-beams resting on the floor.

3. Operational Procedures

3.1. Main Drying Train Preparation

The first step in the preparation of the U-tubes for the main drying train is the determination of the external volumes, in order to correct for the buoyancy effect during a weighing. This is done by weighing the sealed tube first in air, then in water. Once the external volume of a tube has been determined, it need not be done again regardless of the number of tests in which the tube is involved, unless it is broken and repaired.

Prior to filling with desiccant, each U-tube is carefully cleaned with water and detergent, then with a selected series of solvents, and subsequently never handled with bare hands. Whenever a tube must be manipulated, a clean, oil-free chamois skin, or clean, lint-free tissue is used. A length of platinum wire is attached to each tube so that the tube can be suspended from the hook on the arm of the analytical balance for weighing.

The first of the three tubes in the main drying train is freshly filled with anhydrous $\text{Mg}(\text{ClO}_4)_2$ before each test, and the other two are filled with anhydrous P_2O_5 . These latter two tubes pick up only small amounts of moisture, and may be used several times. Care is observed to avoid any contact of the desiccant with the external surface of the tube or with the ground glass stopcock joint. In filling a tube use is made of small glass funnels which protrude into the tube beyond the joint area. In filling a tube with P_2O_5 , small wads of glass wool are coated with desiccant (by immersion into a container filled with P_2O_5) and loosely inserted into the tube through the funnel. In filling a tube with $\text{Mg}(\text{ClO}_4)_2$, the desiccant is packed between glass wool plugs which are inserted at intervals to decrease any tendency for the gas to channel on passage through the tube. The tube is vibrated to eliminate any pockets in the desiccant, and then a short plug of P_2O_5 is added to the exit leg of the U-tube.

Once the tubes are filled, the internal volumes must be determined before they are used, so that a correction may be applied for the mass of gas sealed within the tube during a weighing. This is done by weighing the tube first filled with hydrogen, then with air.

The tubes are weighed prior to the test. Each, in turn, is suspended from one arm of the balance and counterpoised by suspending a tare from the other arm. A tube is weighed at least three times, to obtain an average value. The weighings are made over a period of at least two days.

The tare is a desiccant filled U-tube similar in all respects to the one being weighed. It is subjected to the same procedures, other than insertion into the drying train, as the tubes to be used for the moisture pickup.

3.2. Purging Gas Drying Train Preparation

The three large U-tubes comprising the purging gas drying train may be used many times before maintenance is necessary. If any of the three tubes shows signs of internal discoloration or dampening, it is removed, and cleaned and filled with desiccant by using methods similar to those for the main drying train tubes. Since these large tubes are not weighed, no special precautions are taken with the outside surface, nor are external or internal volumes determined.

3.3. System Preparation

A leak check is made on the main drying train (with glass bridges in place of the U-tubes), pressure switch, both cylinders, and barometer.

A gas, usually tank air, is then passed first through the purging gas drying train, and then on through the main drying train, with the glass bridges still in place. The purge continues for about 16 hr. Near the end of the purge period, the main oil bath is brought to the desired temperature. When temperature control has been reached, the glass bridges are removed, and the main drying train U-tubes re-inserted in their places.

3.4. Test

The test gas is drawn simultaneously through the instrument being calibrated and the gravimetric hygrometer until a predetermined volume has been sampled by the latter. Each time a cylinder in the gravimetric hygrometer is filled with the test gas, measurements are made of the temperature and pressure therein.

3.5. Determination of the Mass of Water Vapor

At the termination of a run, the small U-tubes are removed from the main drying train and the side-arms cleaned with a dry, lint-free tissue to remove any trace of residue left by the "O" ring seals. The tubes are then brought into the balance room, allowed to reach temperature equilibrium (one hour or longer), then momentarily opened and resealed. The internal temperature and pressure is assumed to be that of the balance room at the moment of resealing.

The tubes are weighed in the same manner as before the test. The difference between the weights before and after the test is the mass of water gained by the tube. Since only the weight change is of interest, the true weights of the tube and tare are not determined.

4. Computations, Corrections, Sources of Error, and Accuracy

The mixing ratio is a computed quantity whose magnitude is the ratio of two measurable quantities: the mass of water in a given water vapor-gas sample, and the associated mass of gas. The mass of water is determined directly by weighing. The mass of gas is determined indirectly through a measurement of its volume, and a knowledge of its density.

In principle, the determination of the mixing ratio of a water vapor-gas mixture is a straight forward procedure; in practice, if high accuracy is desired, the determination involves a complex chain of measurements and corrections. There are two types of measurements involved. One type of measurement yields values of parameters that remain fixed for a particular piece of equipment or its components. These parameters need only be determined once; subsequently they may be employed in the computations each time a run is made. The other type of measurement is variable and must be made for each run.

Each of the measurements contributing to the value of the mixing ratio as determined by use of the gravimetric hygrometer will be considered in detail. The nature and magnitude of the corrections that are applied will be examined, the sources of error will be explored, and the accuracy estimated.

4.1. Basis and Nomenclature of Estimates of Accuracy

Although an attempt was made to eliminate or reduce to a negligible value all known sources of systematic error, there remain several that contribute to the uncertainty in the mixing ratio. The nature and magnitude of these will be assessed. All other errors are assumed to be random and are treated as such. The estimate of the accuracy with which the gravimetric hygrometer can measure the mixing ratio of a gas sample will be based on both the systematic and random errors. Standard deviations will be computed, and used as a measure of the random errors. Since the mixing ratio is a computed quantity, the law of propagation of errors [34] will be applied to the random errors to arrive at the standard deviation for the mixing ratio.

$$\text{If } Z = f(z_1, z_2, z_3 \dots) \quad (4.1)$$

where z_1, z_2, z_3, \dots are variables independent in a probability sense, then

$$s^2(Z) = \left[\left(\frac{\partial Z}{\partial z_1} \right)^2 s^2(z_1) + \left(\frac{\partial Z}{\partial z_2} \right)^2 s^2(z_2) + \left(\frac{\partial Z}{\partial z_3} \right)^2 s^2(z_3) + \dots \right] \quad (4.2)$$

and

$$s(Z) = \left[\left(\frac{\partial Z}{\partial z_1} \right)^2 s^2(z_1) + \left(\frac{\partial Z}{\partial z_2} \right)^2 s^2(z_2) + \left(\frac{\partial Z}{\partial z_3} \right)^2 s^2(z_3) + \dots \right]^{1/2} \quad (4.3)$$

where $s^2(Z), s^2(z_1), s^2(z_2), s^2(z_3) \dots$ are the variances and $s(Z), s(z_1), s(z_2), s(z_3) \dots$ are the standard deviations of $Z, z_1, z_2, z_3 \dots$ respectively. If the variable z_n is in turn a function of independent variables $x_1, x_2, x_3 \dots$, then its variance $s^2(z_n)$ and standard deviation $s(z_n)$ will be computed by re-application of (4.2) and (4.3).

This process will be continued as often as necessary.

When the standard deviation $s(z)$ of a single determination of a variate is known, then the standard deviation of the average \bar{z} is given by

$$s(\bar{z}) = s(z)/\sqrt{n} \quad (4.4)$$

where n trials are used to compute \bar{z} .

If the standard deviation of a particular parameter or measured quantity y_n is unknown, or cannot be computed from experimental data, then an attempt will be made to estimate its maximum random error Δy_n based on experience or other criteria. If y_n is a function of independent parameters $y_1, y_2, y_3 \dots$ the maximum random error Δy_n will be assumed given by

$$\Delta y_n = \Delta y_1 + \Delta y_2 + \Delta y_3 + \dots \quad (4.5)$$

where $\Delta y_1, \Delta y_2, \Delta y_3 \dots$ are the maximum errors of $y_1, y_2, y_3 \dots$ respectively and where the magnitudes of the terms are added irrespective of sign. The standard deviation $s(y_n)$ will be taken as $1/3 \Delta y_n$ and will be so used in eqs (4.2) and (4.3).

When both an experimental and a calculated value of the standard deviation of a quantity are available for substitution into the above equations, the larger value will be used.

Consider now the mixing ratio eq (1.1). The standard deviation of the mixing ratio, $s(r)$ is given by

$$s(r) = \left[\left(\frac{\partial r}{\partial M} \right)^2 s^2(M) + \left(\frac{\partial r}{\partial V} \right)^2 s^2(V) + \left(\frac{\partial r}{\partial \rho} \right)^2 s^2(\rho) \right]^{1/2} \quad (4.6)$$

4.2. Measurement of the Mass of Water Vapor

The mass of the water vapor absorbed by the desiccant in a U-tube depends not only on the face values of the weights used in the initial and final weighings but also on such factors as the buoyancy

effect on U-tube, tare and weights, the water vapor adsorption on the external U-tube, tare and weight surfaces, static charge on U-tube and tare, convective air currents within the balance case, handling and treatment of U-tube and tare, mass of internal gas in the U-tube, and incompleteness of absorption by the desiccant.

The mass of water vapor, m , absorbed by the desiccant in a U-tube is given by

$$m = W_f - W_i + C_w + C_b + C_a + C_g + C_i \quad (4.7)$$

where

W_f = sum of face values of weights necessary to bring the balance to equilibrium after a run with the U-tube on one pan and the tare on the other pan, g

W_i = sum of face values of weights necessary to bring the balance to equilibrium before a run with the U-tube on one pan and the tare on the other pan, g

C_w = correction for calibration of weights, g

C_b = correction for the effect of air buoyancy on U-tube, tare and weights, g

C_a = correction for water vapor absorbed on external surfaces of U-tube, tare and weights, g

C_g = correction for mass of gas sealed in the U-tube, g

C_i = correction for incompleteness of water vapor absorption by the desiccant, g.

The mass of water vapor, M , admixed with a given volume or mass of gas is the sum of the increases in masses of the first two tubes of the three-tube main absorption train, that is

$$M = m_1 + m_2 \quad (4.8)$$

where

m_1 = increase in mass of the first tube, g,

m_2 = increase in mass of the second tube, g.

About 0.6 g of water is collected in the first tube and 0.2 mg is collected in the second tube in a typical mixing ratio determination.

Each of the correction terms C_w , C_b , C_a , and C_g given in eq (4.7) are differences between the corresponding correction for the initial and final weighings; for example, $C_b = C_{bf} - C_{bi}$ where C_{bi} is a buoyancy correction applied to the initial weighing and C_{bf} is a buoyancy correction applied to the final weighing.

The sum of the corrections applied to the difference $W_f - W_i$ for any tube is of the order of 2 mg. The corrections constitute nominally one-third of 1 percent of the total weight.

The standard deviation of m , $s(m)$, by application of eq (4.3) is

$$s(m) = \left[s^2(W_f) + s^2(W_i) + s^2(C_w) + s^2(C_b) + s^2(C_a) + s^2(C_g) + s^2(C_i) \right]^{1/2} \quad (4.9)$$

and the standard deviation of M , $s(M)$, is therefore

$$s(M) = \left[s^2(m_1) + s^2(m_2) \right]^{1/2} \quad (4.10)$$

The above corrections, the errors involved in applying these corrections, and uncertainties due to other factors are discussed in detail below.

a. Balance and Weights

The 100-g capacity equal-arm semi-micro balance used to weigh the U-tubes has a reciprocal sensitivity of approximately 0.02 mg/div. It is possible to estimate to 0.1 division, that is, to the nearest 0.002 mg. Pointer deflections are observed through a telescope. The length ratio of the right to left balance arm is 1.000003. Transposition weighings are used, which compensate for the inequality in arm length. Based on repeated weighing experiments with stainless steel weights of 50- and 100-g capacity, it is estimated that the variability of the balance, that is, the standard deviation of a single transposition weighing, is $s(W_f) = s(W_i) = 0.011$ mg.

A set of class M weights [35] is used with the balance. The weights of face values 1 g to 100 g are fabricated from Brunton metal and have a stated density at 20 °C of 7.89 g/cm³. The weights of face values 1 mg to 500 mg are fabricated from an alloy of 80 percent Ni and 20 percent Cr composition and have a stated density at 20 °C of 8.39 g/cm³.

These weights were calibrated by the Mass Section of the National Bureau of Standards. The individual weights up through the 0.5 g denomination are provided with corrections to the nearest 0.0001 mg, the individual weights from 1 through 10 g are provided with corrections to the nearest 0.001 mg, and the individual weights from 20 through 100 g are provided with corrections to the nearest 0.01 mg. The maximum uncertainties are ten times the above precision [35]; the standard deviations are assumed to be one-third the maximum uncertainties (see sec. 4.1).

The differences between the masses of the U-tubes and the tares never exceed 10 g. No more than three weights of denomination one through ten grams, and no more than eight weights of denomination less than one gram, are used. The correction for a single weighing never exceeds 0.125 mg and for a differential weighing never exceeds 0.06 mg. Using the numbers three and eight, along with the accuracy criteria for class M weights, the error in the correction to the larger weights expressed as a standard deviation is $\sqrt{3}(3 \times 10^{-6})$ or 5.2×10^{-6} g, and for the smaller weights is $\sqrt{8}(3 \times 10^{-7})$ or 10^{-6} g. Thus the standard deviation of the correction for the calibration of the weights for single weighing is nominally 5.3×10^{-6} g, and for a differential weighing $s(C_w)$ is $\sqrt{2}(5.3 \times 10^{-6})$ g or 7.5×10^{-6} g.

b. Buoyancy Correction

With an equal-arm balance, the use of a tare is normally the preferred procedure for precision

differential weighing since it tends to compensate not only for the effect of air buoyancy on the U-tube and tare, but also for other possible changes in tube weight due to handling, dust accumulation, and moisture adsorption on the external surfaces. However, since the external volumes of the tare and U-tube are not precisely equal, and since barometric pressure changes may on occasion introduce significant density changes, a buoyancy correction is applied to the differential weighing. This correction is given by

$$C_b = \left[\frac{W_{L_f}}{D_L} + \frac{W_{S_f}}{D_S} + V_U - V_T \right] \rho_f - \left[\frac{W_{L_i}}{D_L} + \frac{W_{S_i}}{D_S} + V_U - V_T \right] \rho_i \quad (4.11)$$

where

ρ_i = density of the ambient air at the time of the initial weighing, g/cm³

ρ_f = density of the ambient air at the time of the final weighing, g/cm³

V_T = external volume of the tare, cm³

V_U = external volume of the unknown U-tube, cm³

W_{L_i} = calibrated values of weights 1 g and above at the time of the initial weighing, g

W_{L_f} = calibrated values of weights 1 g and above at the time of the final weighing, g

W_{S_i} = calibrated value of weights less than 1 g on the pan at the time of the initial weighing, g

W_{S_f} = calibrated values of weights less than 1 g on the pan at the time of the final weighing, g

D_L = density of weights 1 g and above, g/cm³

D_S = density of weights less than 1 g, g/cm³.

Although C_b can be as large as 0.5 mg, it normally is of the order of 0.15 mg.

Using the law of propagation of errors, the uncertainty in the buoyancy correction C_b is computed from the equation

$$s(C_b) = \left[\left(\frac{\partial C_b}{\partial \rho_f} \right)^2 s^2(\rho_f) + \left(\frac{\partial C_b}{\partial \rho_i} \right)^2 s^2(\rho_i) + \left(\frac{\partial C_b}{\partial V_T} \right)^2 s^2(V_T) + \left(\frac{\partial C_b}{\partial V_U} \right)^2 s^2(V_U) + \left(\frac{\partial C_b}{\partial W_{L_i}} \right)^2 s^2(W_{L_i}) + \left(\frac{\partial C_b}{\partial W_{L_f}} \right)^2 s^2(W_{L_f}) + \left(\frac{\partial C_b}{\partial W_{S_i}} \right)^2 s^2(W_{S_i}) + \left(\frac{\partial C_b}{\partial W_{S_f}} \right)^2 s^2(W_{S_f}) + \left(\frac{\partial C_b}{\partial D_L} \right)^2 s^2(D_L) + \left(\frac{\partial C_b}{\partial D_S} \right)^2 s^2(D_S) \right]^{1/2} \quad (4.12)$$

where

$$\frac{\partial C_b}{\partial \rho_f} = \frac{W_{L_f}}{D_L} + \frac{W_{S_f}}{D_S} + V_U - V_T \quad (4.13)$$

$$\frac{\partial C_b}{\partial \rho_i} = \frac{W_{L_i}}{D_L} + \frac{W_{S_i}}{D_S} + V_U - V_T \quad (4.14)$$

$$\frac{\partial C_b}{\partial V_T} = \rho_i - \rho_f \quad (4.15)$$

$$\frac{\partial C_b}{\partial V_U} = \rho_f - \rho_i \quad (4.16)$$

$$\frac{\partial C_b}{\partial W_{L_i}} = -\frac{\rho_i}{D_L} \quad (4.17)$$

$$\frac{\partial C_b}{\partial W_{L_f}} = -\frac{\rho_f}{D_L} \quad (4.18)$$

$$\frac{\partial C_b}{\partial W_{S_i}} = -\frac{\rho_i}{D_S} \quad (4.19)$$

$$\frac{\partial C_b}{\partial W_{S_f}} = -\frac{\rho_f}{D_S} \quad (4.20)$$

$$\frac{\partial C_b}{\partial D_S} = \frac{W_{S_i} \rho_i}{D_S^2} - \frac{W_{S_f} \rho_f}{D_S^2} \quad (4.21)$$

$$\frac{\partial C_b}{\partial D_L} = \frac{W_{L_i} \rho_i}{D_L^2} - \frac{W_{L_f} \rho_f}{D_L^2} \quad (4.22)$$

Each of the terms in eqs (4.11) and (4.12) will be investigated in the following subsections.

Air Density in the Balance Case.—The density of the air in g/cm³ is computed from the relation

$$\rho = \rho_0 \times \frac{273.16}{T} \times \frac{(B - 0.003780 e_s RH)}{760} \quad (4.23)$$

where T is the absolute temperature in deg K, B is the barometric pressure in mm Hg at standard gravity and 0 °C, e_s is the saturation vapor pressure of water at T in mm Hg at standard gravity and 0 °C, RH is the relative humidity in percent at T , and ρ_0 , the density of air, at a pressure of 760 mm Hg and a temperature of 273.16 °K, is 1.29304×10^{-3} g/cm³ (sec. 4.4.a).

The ambient temperature in the balance room is maintained constant at about 25 °C. The relative humidity changes with the seasons of the year, but rarely exceeds 50 percent. The barometric pressure fluctuates between 740 to 770 mm Hg depending on external weather conditions. As a result the air density varies from 1.150×10^{-3} to 1.200×10^{-3} g/cm³; however, the changes in density between initial and final weighings of a U-tube are usually much smaller in magnitude, even though the elapsed time between an initial and final weighing may be as long as two weeks.

The standard deviation of the air density follows from the equation

$$s(\rho) = \left[\left(\frac{\partial \rho}{\partial T} \right)^2 s^2(T) + \left(\frac{\partial \rho}{\partial B} \right)^2 s^2(B) + \left(\frac{\partial \rho}{\partial RH} \right)^2 s^2(RH) + \left(\frac{\partial \rho}{\partial e_s} \right)^2 s^2(e_s) \right]^{1/2} \quad (4.24)$$

where

$$\frac{\partial \rho}{\partial T} = -1.29304 \times 10^{-3} \times \frac{273.16}{T^2} \times \frac{(B - 0.003780 e_s RH)}{760} \quad (4.25)$$

$$\frac{\partial \rho}{\partial B} = 1.29034 \times 10^{-3} \times \frac{273.16}{T} \times \frac{1}{760} \quad (4.26)$$

$$\frac{\partial \rho}{\partial RH} = -1.29304 \times 10^{-3} \times \frac{273.16}{T} \times \frac{0.003780 e_s}{760} \quad (4.27)$$

$$\frac{\partial \rho}{\partial e_s} = -1.29304 \times 10^{-3} \times \frac{273.16}{T} \times \frac{0.003780 RH}{760} \quad (4.28)$$

It can be shown that the uncertainty in ρ_0 (sec. 4.4.a) has a negligible effect on ρ . Hence in this section ρ_0 will be assumed to be exact. The ratio of the compressibility of moist air at standard conditions to that near room temperatures and pressures is assumed equal to 1 for the present purposes. The error thus introduced in the density is about 4 parts in 10^4 [36] which is insignificant in its effect on C_b .

The temperature in the balance case is measured with a calibrated 0 ° to 50 °C mercury-in-glass thermometer. This thermometer has a scale graduated to 0.1 deg C divisions which may be read by estimation to 0.01 deg C. Scale corrections to the nearest 0.01 °C are supplied to the readings. The maximum uncertainty, due to scale error, reading error, lack of repeatability, room temperature fluctuations, and influence of observer is estimated to be 0.2 °C. The standard deviation $s(T)$ will therefore be assumed equal to 0.07 °C.

The pressure in the balance is assumed equal to that in the balance room and is read with a precision aneroid barometer. The scale is subdivided into 0.2 mm Hg divisions so that readings may be estimated to 0.02 mm Hg. This instrument was calibrated in 1950, 1958, 1960, and 1962 against the NBS standard mercury barometer which has an uncertainty of 0.03 mm Hg. From the scatter of calibration points about the best curve drawn through the data in the range from 730 to 770 mm Hg, it is concluded that the maximum repeatability error is 0.05 mm Hg. The calibration curves shifted as much as 0.06 mm Hg during the eight year period between the first and second calibration, as much as 0.15 mm Hg during the two year period between the second and third calibrations, and as much as 0.10 mm Hg during the two year period between the third and fourth calibrations. The drift has been monotonic with time. If the instrument is recalibrated at periodic intervals, and if a correction is also applied for the anticipated drift during that

interval, then it will be assumed that the maximum residual uncertainty due to drift is 0.04 mm Hg. Although the aneroid barometer is observed at the nominal midpoint in time of the weighing procedure, there may be micro-barometric fluctuations during the procedure. Based on experience, it is concluded that the maximum error due to this factor is 0.13 mm Hg. The sum of the individual uncertainties yields a total maximum error of 0.27 mm Hg. The standard deviation $s(B)$ is therefore assumed to be 0.09 mm Hg.

The partial pressure of the water vapor in the air (which is determined from the relative humidity and saturation pressure at the air temperature) is assumed to be the same both in the balance room and balance case. Hence, the relative humidity is measured in the balance room, eliminating the necessity of placing a humidity sensor in the balance case.

The saturation vapor pressure of water is a function solely of temperature. Given the temperature, the corresponding saturation vapor pressure, e_s , may be computed or, preferably, obtained from tables. For purposes of this computation, the values tabulated in the Smithsonian Meteorological Tables [37] may be accepted as correct. Any error in e_s is therefore dependent only on the error in the temperature measurement.

A thermometer similar in all respects to the one in the balance case is used to determine the room temperature. The maximum uncertainty of this temperature reading is also 0.2 °C. The equivalent error in e_s , at the nominal balance room temperature of 25 °C, is 0.28 mm Hg. The standard deviation, $s(e_s)$ is assumed to be 0.09 mm Hg.

The relative humidity in the balance room is measured with an electric hygrometer. This instrument has a sensitivity of 0.2 percent RH . It was calibrated in 1956, 1960, and 1962 against the NBS pressure humidity generator [28]. The latter has an accuracy of 1/2 of 1 percent RH . The maximum deviation of the test points from the best curve drawn through the data for any one calibration is 1 percent RH . There was a maximum drift between 1956 and 1960 calibrations of 8 percent RH and between the 1960 and 1962 calibrations of 5 percent. Assuming that this change was linear with time, the drift was then about 2 percent RH per year. If the electric hygrometer is recalibrated periodically, as is intended, and if a correction is made for the anticipated drift, it is estimated that the residual maximum uncertainty due to drift will be about 1/2 percent RH . The sum of the individual maximum errors is 2 percent RH and the standard deviation $s(RH)$ is assumed to be 0.7 percent RH .

The standard deviation of the air density is computed using eqs (4.24) through (4.28) into which are substituted the standard deviations for the independent variables and the nominal values $T=298^\circ K$, $B=750$ mm Hg, $RH=40$ percent, $e_s=23.8$ mm Hg, and $\rho=1.167 \times 10^{-3}$ g/cm³. The steps are listed in table 1 together with the result.

TABLE 1. Standard deviation of the air density for water vapor mass determination

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial \rho}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right)^2 s^2(z_n)$
T	$3.9 \times 10^{-6} \text{ g/cm}^3 / ^\circ\text{K}$	$0.07 ^\circ\text{K}$	$0.27 \times 10^{-6} \text{ g/cm}^3$	$0.0729 \times 10^{-12} \text{ g}^2/\text{cm}^6$
B	$1.6 \times 10^{-6} \text{ g/cm}^3/\text{mm Hg}$	0.09 mm Hg	$0.14 \times 10^{-6} \text{ g/cm}^3$	$0.0196 \times 10^{-12} \text{ g}^2/\text{cm}^6$
RH	$0.15 \times 10^{-6} \text{ g/cm}^3/\% RH$	$0.7 \% RH$	$0.10 \times 10^{-6} \text{ g/cm}^3$	$0.0100 \times 10^{-12} \text{ g}^2/\text{cm}^6$
c_e	$0.24 \times 10^{-6} \text{ g/cm}^3/\text{mm Hg}$	0.09 mm Hg	$0.022 \times 10^{-6} \text{ g/cm}^3$	$0.0005 \times 10^{-12} \text{ g}^2/\text{cm}^6$

$$s^2(\rho) = 0.1030 \times 10^{-12} \text{ g}^2/\text{cm}^6$$

$$s(\rho) = 0.32 \times 10^{-6} \text{ g/cm}^3$$

The standard deviation of the air density is $0.32 \times 10^{-6} \text{ g/cm}^3$.

External Volume of U-Tube.—The external volume of each U-tube was determined by weighing in air and in distilled water. An equal-arm balance (not the one used in the balance room) was mounted on a table, over an open cylinder of distilled water. A stainless steel wire was attached to the right pan and a 29.4-g weight suspended from the end of the wire and immersed in the water. A U-tube was then placed on the right pan and counter-balance with weights on the left pan. This provided the U-tube weight in air. The U-tube was then attached to the wire, immersed in the cylinder of water, and again weighed. During these operations, the glass stopcocks were kept in their closed positions. Precautions were taken to insure that the U-tube side arms were filled with water and did not contain trapped air.

Consider the case where the U-tube is weighed in air. Let L be the length of the balance arms, W_1 the weight suspended from the left pan, W_0 the weight suspended from the right pan via the wire and immersed in the water, and W_g the weight of the sealed U-tube, also suspended from the right pan. The weight W_1 and the U-tube are buoyed up by displaced air of density ρ_1 while the weight W_0 is buoyed up by displaced water of density d_1 . If the density of W_1 is given by D and of W_0 by D_0 , and if the external U-tube volume at the ambient temperature is given by V_0 , then it follows that

$$W_1 L - \frac{W_1 \rho_1 L}{D} = W_g L - V_0 \rho_1 L + W_0 L - \frac{W_0 d_1 L}{D_0} \quad (4.29)$$

In an analogous manner, when the U-tube is weighed immersed in water, the equilibrium equation is as follows:

$$W_2 L - W_2 \frac{\rho_2}{D} L = W_g L - V_0 d_2 L + W_0 L - W_0 \frac{d_2}{D_0} L \quad (4.30)$$

where subscript 2 refers to the final conditions, i.e., the weighing operation with the U-tube suspended in water. Combining these two equations

yields

$$V_0 = \frac{W_1 - W_2}{(d_2 - \rho_1)} + \frac{W_2 \frac{\rho_2}{D} - W_1 \frac{\rho_1}{D}}{(d_2 - \rho_1)} - \frac{W_0}{D_0} (d_2 - d_1) \quad (4.31)$$

The external volumes of the U-tubes and tares are nominally 65 cm^3 . The U-tubes and tares do not differ in external volume by more than 10 cm^3 . For most combinations of U-tubes and tares the difference in external volumes is of the order of 2 to 3 cm^3 .

The contribution to the buoyancy correction C_b due to this volume difference rarely exceeds 0.4 mg . The magnitude of the uncertainty in the measurement of the external volume and the effect of this uncertainty on the buoyancy correction will now be investigated.

Since the external volume is a function of independent variables, the law of propagation of error is used to predict the accuracy of its determination. The standard deviation of the external U-tube volume is therefore

$$s(V_0) = \left[\left(\frac{\partial V_0}{\partial \rho_1} \right)^2 s^2(\rho_1) + \left(\frac{\partial V_0}{\partial \rho_2} \right)^2 s^2(\rho_2) + \left(\frac{\partial V_0}{\partial d_1} \right)^2 s^2(d_1) + \left(\frac{\partial V_0}{\partial d_2} \right)^2 s^2(d_2) + \left(\frac{\partial V_0}{\partial D} \right)^2 s^2(D) + \left(\frac{\partial V_0}{\partial D_0} \right)^2 s^2(D_0) + \left(\frac{\partial V_0}{\partial W_1} \right)^2 s^2(W_1) + \left(\frac{\partial V_0}{\partial W_2} \right)^2 s^2(W_2) + \left(\frac{\partial V_0}{\partial W_0} \right)^2 s^2(W_0) \right]^{1/2} \quad (4.32)$$

where

$$\frac{\partial V_0}{\partial \rho_1} = \frac{(W_1 - W_2)}{(d_2 - \rho_1)^2} + \frac{W_2 \rho_2 - W_1 \rho_1 - W_1 (d_2 - \rho_1)}{D(d_2 - \rho_1)^2} - \frac{W_0 (d_2 - d_1)}{D_0 (d_2 - \rho_1)^2} \quad (4.33)$$

$$\frac{\partial V_0}{\partial \rho_2} = \frac{W_2}{D(d_2 - \rho_1)} \quad (4.34)$$

$$\frac{\partial V_0}{\partial d_1} = \frac{W_0}{D_0(d_2 - \rho_1)} \quad (4.35)$$

$$\frac{\partial V_0}{\partial d_2} = \frac{(W_2 - W_1)}{(d_2 - \rho_1)^2} - \frac{(W_2 \rho_2 - W_1 \rho_1)}{D(d_2 - \rho_1)^2} - \frac{W_0}{D_0(d_2 - \rho_1)} + \frac{W_0(d_2 - d_1)}{D_0(d_2 - \rho_1)^2} \quad (4.36)$$

$$\frac{\partial V_0}{\partial D} = -\frac{(W_2 \rho_2 - W_1 \rho_1)}{D^2(d_2 - \rho_1)} \quad (4.37)$$

$$\frac{\partial V_0}{\partial D_0} = \frac{W_0(d_2 - d_1)}{D_0^2(d_2 - \rho_1)} \quad (4.38)$$

$$\frac{\partial V_0}{\partial W_1} = \frac{D - \rho_1}{D(d_2 - \rho_1)} \quad (4.39)$$

$$\frac{\partial V_0}{\partial W_2} = -\frac{(D - \rho_2)}{D(d_2 - \rho_1)} \quad (4.40)$$

$$\frac{\partial V_0}{\partial W_0} = -\frac{(d_2 - d_1)}{D_0(d_2 - \rho_1)} \quad (4.41)$$

In order to obtain a numerical value for $s(V_0)$, each of the terms on the right-hand side of (4.32) must be evaluated.

Consider first the air density. It was determined each time a weighing was made by measuring the ambient temperature, pressure, and relative humidity and substituting these values into (4.23). The standard deviation of the air density, estimated in a fashion similar to that described in the sec. on p. 10, is 0.42×10^{-6} g/cm³.

Consider next the density of water. Experimental determinations of the density of compressed water (water under a total pressure higher than that of its pure saturated vapor) at a pressure of one atmosphere were made by Chappuis [38] and by Thiesen, Scheel, and Diesselhorst [39]. Stott and Bigg [40] compiled a table based on the average of these two sets of values. Tilton and Taylor [41] then derived a new formula to fit the observed values of Chappuis more closely. The Tilton and Taylor tabulation was used in these external volume experiments. Over the temperature range 0° to 40°C, the published values of density are given to one part in 10 million. At and near 25°C, the nominal temperature of the water during the external U-tube volume experiments, the densities as given by Thiesen et al., and by Chappuis differ from that of Tilton and Taylor by no more than 5 ppm.

The density of water is a function not only of the temperature, but also of the ambient pressure, the dissolved gases in the water, and the solid impurities in the water.

The temperature of the water was measured with a calibrated mercury-in-glass thermometer. The water, approximately 25 liters in volume, was contained in a glass cylinder and was located beneath the balance in a room which fluctuated and drifted in

temperature. No attempt was made to stir the water so that there undoubtedly were temperature differentials throughout the liquid volume. It is estimated that the average temperature of the water in which the U-tube was immersed could have differed from the measured temperature by as much as 0.4 deg C. At a nominal temperature of 25°C, the equivalent maximum uncertainty in the density of water was 91×10^{-6} g/cm³.

The variation of the density of water with pressure, in the temperature range between 20° to 30°C, is about 44×10^{-6} g/cm³/atm [42]. Ambient atmospheric pressure can vary between 740 and 770 mm Hg, hence the maximum density variation due to this factor is about 2×10^{-6} g/cm³.

Absorbed air in the water reduces the water density; at 20°C the density of water saturated with air has been reported to be reduced by as little as 0.2×10^{-6} to as much as 2×10^{-6} g/cm³ [42].

Another source of error arises from the presence of solid impurities in the water. However, the solid impurities in the particular distilled water used in these experiments probably did not exceed 5 ppm, a value inferred from other uses. Assuming that the average density of these impurities was 8 g/cm³, then the resultant maximum uncertainty in the water density was 35×10^{-6} g/cm³.

Totaling the known uncertainties gives rise to a maximum value of 135×10^{-6} g/cm³. Applying eq 4.5, the standard deviation is 45×10^{-6} g/cm³.

A set of class S nickel-plated metric weights was used to weigh the U-tube both in air and immersed in water. For the purposes of this work, the uncertainties in the masses of the weights W_1 and W_2 , arising from the weight calibration, are negligible and were ignored. The density D of the weights was assumed to be that of normal brass, which is 8.4 g/cm³ at 0°C. The material of the fractional gram weights was either platinum or aluminum; however, no attempt was made to differentiate these weights from the brass weights in the computations involving the density of the weights. It is estimated, therefore, that the maximum error in the density of the weights is 0.1 g/cm³. However, the effect of this error on V_0 is negligible.

A thick wire, probably of lead, was twisted into a compact ball and used as the weight W_0 . The nominal apparent mass of the ball, together with that of the stainless steel support wire and hook, was 29.4 g. The density D_0 was assumed to be 11.3 g/cm³. Since these values were only involved in a small correction to V_0 (the last term on the right-hand side of eq (4.31), it was considered unnecessary to have accuracies greater than 0.1 g in W_0 and 0.3 g/cm³ in D_0 . The resultant error in V_0 is systematic but negligible.

The estimated standard deviations for W_1 and W_2 are based on observations of the variability of the balance with loads of 98 g (W_1) and 33 g (W_2) and without load on the pans. It was determined that the maximum variability with a 98 g load was 36 mg, and with a 33 g load was 30 mg. The corresponding

TABLE 2. Standard deviation of external U-tube volume

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial V_0}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_0}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial V_0}{\partial z_n}\right)^2 s^2(z_n)$
ρ_1	53.9 cm ³ /g	0.42×10^{-6} g/cm ³	22.6×10^{-6} cm ³	negligible
ρ_2	3.8 cm ³ /g	0.42×10^{-6} g/cm ³	1.7×10^{-6} cm ³	negligible
d_1	2.6 cm ³ /g	45×10^{-6} g/cm ³	117×10^{-6} cm ³	negligible
d_2	68.1 cm ³ /g	45×10^{-6} g/cm ³	3064×10^{-6} cm ³	9.4×10^{-6} cm ⁶
W_1	1.0 cm ³ /g	0.013 g	0.013 cm ³	169×10^{-6} cm ⁶
W_2	1.0 cm ³ /g	0.010 g	0.010 cm ³	100×10^{-6} cm ⁶

$$s^2(V_0) = 278 \times 10^{-6} \text{ cm}^6$$

$$s(V_0) = 0.017 \text{ cm}^3$$

standard deviations are assumed to be 13 mg and 10 mg.

Substituting nominal values $W_1 = 98$ g, $W_2 = 33$ g, $W_0 = 29.4$ g, $d_1 = d_2 = 0.997$ g/cm³, $D = 8.4$ g/cm³, $D_0 = 11.3$ g/cm³, $\rho_1 = \rho_2 = 0.00116$ g/cm³, $d_2 - d_1 = 0.00025$ g/cm³, and the standard deviations for each independent variable into eqs (4.33) through (4.41) yields 0.017 cm³ as the computed standard deviation of the external volume $s(V_0)$. The computations and result are shown in table 2.

The major source of error in the measurement of V_0 was due to the variability of the balance. There was a small contribution from the uncertainty in the density of the water, $s(d_2)$, during the weighing operation with the U-tube immersed in the water; errors contributed by the other parameters were negligible.

Except for four U-tubes, only a single experimental determination was made of the external volume of each U-tube. For these four U-tubes, the measurement on each tube was repeated 3 to 5 times. By pooling [43] the data thus obtained, it was calculated that the standard deviation of a single experimental determination of the external volume of a U-tube was 0.036 cm³. This is of the same order of magnitude as the estimate of standard deviation (0.017 cm³) based on the law of propagation of errors.

In the experimental determination of V_0 , no attempt was made to control either the temperature of the ambient air or the water in which the U-tube was immersed. The temperature to which the U-tube is subjected in the balance room during the

weighing procedure, involved in a run, will usually differ from that which prevailed during the measurement of V_0 . The following correction, C_E , may be applied to compensate for the change in the external volume due to the change in temperature.

$$C_E = V_0 \alpha \Delta t \quad (4.42)$$

where

V_0 = external volume at the calibration temperature, cm³

α = coefficient of volume expansion of Pyrex glass, cm³/cm³/°C

Δt = difference between the calibration and weighing temperatures, °C.

The average coefficient of linear expansion of Pyrex glass over the range 20 to 300 °C is 33×10^{-7} cm/cm/°C [44]. The coefficient of volume expansion is considered to be three times as large or 9.9×10^{-6} cm³/cm³/°C. Since the nominal volume, V_0 , of a U-tube is 65 cm³, and Δt does not exceed 4 °C, $C_E \geq 26 \times 10^{-4}$ cm³. Since the maximum air density change between initial and final weighings is 5×10^{-5} g/cm³ (see sec. on p. 10), the error in the buoyancy correction, arising from the thermal expansion of Pyrex, does not exceed $26 \times 10^{-4} \times 5 \times 10^{-5} = 13 \times 10^{-8}$ g, which is negligible. Therefore this correction is not applied.

Weights.—The material, density, and accuracy of the weights were discussed in sec. 4.2a. The maximum uncertainty in density is estimated to be 0.03 g/cm³. This contributes a systematic but negligible error.

TABLE 3. Standard deviation of the buoyancy correction for the water vapor mass determination

Independent variable	Partial derivative	Standard deviation		Variance
Z_n	$\frac{\partial C_b}{\partial Z_n}$	$s(Z_n)$	$\left(\frac{\partial C_b}{\partial Z_n}\right) s(Z_n)$	$\left(\frac{\partial C_b}{\partial Z_n}\right)^2 s^2(Z_n)$
ρ_i	11.36 cm ³	0.32×10^{-6} g/cm ³	3.635×10^{-6} g	13.213×10^{-12} g ²
ρ_f	11.36 cm ³	0.32×10^{-6} g/cm ³	3.635×10^{-6} g	13.213×10^{-12} g ²
V_T	10^{-4} g/cm ³	0.04 cm ³	4.00×10^{-6} g	16.000×10^{-12} g ²
V_U	10^{-4} g/cm ³	0.04 cm ³	4.00×10^{-6} g	16.000×10^{-12} g ²
W_{L_i}	0.00015	5.2×10^{-6} g	Negligible	Negligible
W_{L_f}	0.00015	5.2×10^{-6} g	Negligible	Negligible
W_{S_i}	0.00014	10^{-6} g	Negligible	Negligible
W_{S_f}	0.00014	10^{-6} g	Negligible	Negligible

$$s^2(C_b) = 58.426 \text{ g}^2$$

$$s(C_b) = 7.6 \times 10^{-6} \text{ g}$$

Error in the Buoyancy Correction.—An estimate may now be made of the standard deviation of the buoyancy correction $s(C_b)$. For this computation, the following nominal values of the independent variables will be used: $V_U - V_T = 10 \text{ cm}^3$, $\rho_f = \rho_i = 0.00116 \text{ g/cm}^3$, $W_{L_f} = W_{L_i} = 10 \text{ g}$, $D_L = 7.9 \text{ g/cm}^3$, $D_S = 8.4 \text{ g/cm}^3$, $\rho_f - \rho_i = 10^{-4} \text{ g/cm}^3$, $W_{s_f} = W_{s_i} = 0.5 \text{ g}$.

These values, as well as the standard deviations of the independent variables, are substituted in eqs (4.13) through (4.22). The calculations and the result are shown in table 3. The experimental standard deviation of the U-tube external volume, 0.04 cm^3 , is used in the calculations, since it is the larger of the calculated and experimental values. The standard deviation of the buoyancy correction is $7.6 \times 10^{-6} \text{ g}$.

c. Water Vapor Adsorption on External U-Tube Surface

Water vapor is adsorbed by metal and glass surfaces in proportion to the ambient relative humidity. Since the balance is symmetrical in its construction, the adsorption on the arms, pans and other components will tend to compensate and may therefore be neglected. The adsorption on the metal weights is also negligible in magnitude. Barett, Bernie, and Cohen [45] give the weight of water vapor adsorbed by nearly pure silica at 30.2°C , as a function of relative humidity. It is monotonic, and at an RH of 50 percent, $0.025 \mu\text{g/cm}^2$ is adsorbed.

Razouk and Salem [46] performed similar experiments with a glass whose composition is generally as different from Pyrex as the pure silica, only in an opposite sense, that is, less pure silica than Pyrex, and more of the alkaline salts. Their experiments indicate that at an RH of nominally 50 percent (at 30°C and 35°C) the surfaces adsorb $0.2 \mu\text{g/cm}^2$.

Using the compositions of the three materials as a guide, it is assumed that the water adsorption property of Pyrex lies midway between that of pure silica and the glass of Razouk and Salem. Therefore, at 50 percent RH and nominally room temperature, Pyrex is assumed to adsorb $0.11 \mu\text{g/cm}^2$, with a possible systematic error of $\pm 0.11 \mu\text{g/cm}^2$. If the correction were ignored entirely, a maximum possible systematic error of $\pm 0.2 \mu\text{g/cm}^2$ would be introduced.

Since the estimated maximum difference between external U-tube area and tare area is 20 cm^2 , and since the balance room relative humidity is kept below 50 percent, it is seen that the correction may be ignored, leading to a maximum systematic error in U-tube weight of $\pm 4 \mu\text{g}$.

d. Static Charge on U-Tube

Static charge can accumulate on the pans of the balance and on the U-tube. The resultant force that is exerted on the arm of the balance will introduce an error. To avoid or reduce any accumulation of charge, several precautionary measures are observed. The metal balance case is grounded so

that charge on the pan, or other metal parts, will tend to leak off. The glass panels and doors of the case are metalized. Strontium 90 is kept within the balance case, emitting beta rays which ionize the air in the immediate vicinity of the U-tube. In the presence of ionized air there is a greater tendency for any charge on the U-tube to leak off. Since static charge is evidenced by irregularities in the pointer swing, no reading is made until the swing is regular. There may still be residual static charge; the error this contributes, if any, cannot be readily estimated.

e. Handling

Whenever a U-tube is manipulated, as in opening or closing its stopcocks, or in inserting it in the drying train, a clean chamois skin or lens tissue is used to avoid bringing the fingers and hands of the operator into direct contact with the surfaces of the tube. After removal from the drying train, the side arms are cleaned with chamois skin or tissue to remove any residue from the "O" rings. The U-tube, when not in the drying train, or in the balance case, is kept in a covered plastic box to reduce any tendency for dust or dirt to accumulate on the external surfaces. It is dusted with a camel's hair brush prior to suspension from one arm of the balance. The tare is treated similarly. The magnitude of the error arising from handling is difficult to estimate and no attempt will be made to do so here, although it may be inferred from the experimental data subsequently presented (sec. 4.2.j) that handling is one of the largest factors contributing to weighing error.

f. Mass of Internal Gas in U-Tube

The internal volume of an empty U-tube is about 50 cm^3 . When filled with desiccant, the unoccupied volume is about 30 cm^3 . If air occupies this volume, then the weight of this air is part of the weight of the sealed U-tube. Not only can the temperature and pressure of the air at the time the U-tube is sealed differ for the initial and final weighings, but the internal unoccupied volume will decrease due to the absorption of water vapor by the desiccant. Unless a suitable correction is applied, an uncertainty in the difference between initial and final U-tube weights is thereby introduced. This correction may be as large as 1.6 mg .

The correction that must be applied to a differential U-tube weighing due to a change in internal gas density is

$$C_g = V_f \rho_f - V_i \rho_i = V_i (\rho_f - \rho_i) - v \rho_f \quad (4.43)$$

where

V_f = net internal U-tube volume at the time of the final weighing, cm^3

V_i = net internal U-tube volume at the time of the initial weighing, cm^3

ρ_f = density of the gas (usually air) in the U-tube at the time the U-tube is sealed in preparation for the final weighing, g/cm³

ρ_i = density of the gas (usually air) in the U-tube at the time the U-tube is sealed in preparation for the initial weighing, g/cm³

v = decrease in internal volume due to absorbed water, cm³.

The uncertainty in C_g , in terms of standard deviation, is

$$s(C_g) = \left[\left(\frac{\partial C_g}{\partial V_i} \right)^2 s^2(V_i) + \left(\frac{\partial C_g}{\partial v} \right)^2 s^2(v) + \left(\frac{\partial C_g}{\partial \rho_f} \right)^2 s^2(\rho_f) + \left(\frac{\partial C_g}{\partial \rho_i} \right)^2 s^2(\rho_i) \right]^{1/2} \quad (4.44)$$

where

$$\frac{\partial C_g}{\partial V_i} = \rho_f - \rho_i \quad (4.45)$$

$$\frac{\partial C_g}{\partial v} = -\rho_f \quad (4.46)$$

$$\frac{\partial C_g}{\partial \rho_f} = V_i - v \quad (4.47)$$

$$\frac{\partial C_g}{\partial \rho_i} = -V_i \quad (4.48)$$

Density of Gas in U-Tube.—The density of the gas (taken here as dry air) sealed in the U-tube is computed from eq (4.23) in which RH is zero. The standard deviation of the air density, estimated in a similar fashion to that described in the sec. on p. 10, is 0.29×10^{-6} g/cm³.

Initial Internal U-Tube Volume.—To correct for the weight of air sealed in a U-tube, it is necessary to know the volume occupied by the air. If the U-tube is weighed separately with air and then with hydrogen, the initial internal volume can be computed using the equation

$$V_i = \frac{W_a - W_h}{\rho_a - \rho_h} \quad (4.49)$$

where

W_a = mass of U-tube filled with air, g
 W_h = mass of U-tube filled with hydrogen, g

ρ_a = density of air in U-tube, g/cm³
 ρ_h = density of hydrogen in U-tube, g/cm³.

From the law of propagation of errors, the uncertainty in internal volume is

$$s(V_i) = \left[\left(\frac{\partial V_i}{\partial W_a} \right)^2 s^2(W_a) + \left(\frac{\partial V_i}{\partial W_h} \right)^2 s^2(W_h) + \left(\frac{\partial V_i}{\partial \rho_a} \right)^2 s^2(\rho_a) + \left(\frac{\partial V_i}{\partial \rho_h} \right)^2 s^2(\rho_h) \right]^{1/2} \quad (4.50)$$

where

$$\frac{\partial V_i}{\partial W_a} = \frac{1}{\rho_a - \rho_h} \quad (4.51)$$

$$\frac{\partial V_i}{\partial W_h} = -\frac{1}{\rho_a - \rho_h} \quad (4.52)$$

$$\frac{\partial V_i}{\partial \rho_a} = -\frac{W_a - W_h}{(\rho_a - \rho_h)^2} \quad (4.53)$$

$$\frac{\partial V_i}{\partial \rho_h} = \frac{W_a - W_h}{(\rho_a - \rho_h)^2} \quad (4.54)$$

The standard deviation of the internal air density is 0.29×10^{-6} g/cm³ (see preceeding sec.). An analysis for the internal hydrogen density, the steps of which are shown in table 4, yields a standard deviation of 2×10^{-8} g/cm³.

For the purposes of this computation, the experimentally determined standard deviation of the mass change of a single U-tube based on flushing with dry gas, given in sec. 4.2.j will be used. Thus

$$s(W_a) = s(W_h) = 0.08 \text{ mg.}$$

The appropriate errors and nominal values are substituted in eqs (4.52) through (4.55) to yield $s(V_i) = 0.11$ cm³, as shown in table 5.

Change in Internal U-Tube Volume.—The internal volume of a U-tube is decreased between initial and final weighings because of the absorbed water.

The first U-tube of the drying train absorbs on the order of 0.6 g of water vapor. This tube contains magnesium perchlorate. When a gram-mole of $\text{Mg}(\text{ClO}_4)_2$ absorbs water, the $\text{Mg}(\text{ClO}_4)_2$ may combine with 2, 4, or 6 gram-moles of water [47], depending on the water available.

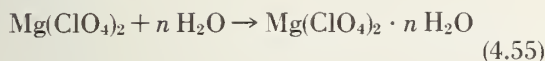
TABLE 4. Standard deviation of hydrogen density in sealed U-tube

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial \rho_h}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho_h}{\partial z_n} \right) s(z_n)$	$\left(\frac{\partial \rho_h}{\partial z_n} \right)^2 s^2(z_n)$
T	0.27×10^{-6} g/cm ³ /°K	0.07 °K	1.9×10^{-8}	3.6×10^{-16} g ² /cm ⁶
B	0.11×10^{-6} g/cm ³ /mm Hg	0.06 mm Hg	0.66×10^{-8}	0.44×10^{-16} g ² /cm ⁶
				$s^2(\rho_h) = 4.0 \times 10^{-16}$ g ² /cm ⁶ $s(\rho_h) = 2 \times 10^{-8}$ g/cm ³

TABLE 5. Standard deviation of initial internal U-tube volume

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial V_i}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_i}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial V_i}{\partial z_n}\right)^2 s^2(z_n)$
W_a	$0.93 \times 10^3 \text{ cm}^3/\text{g}$	$80 \times 10^{-6} \text{ g}$	$74 \times 10^{-3} \text{ cm}^3$	$5476 \times 10^{-6} \text{ cm}^6$
W_h	$0.93 \times 10^3 \text{ cm}^3/\text{g}$	$80 \times 10^{-6} \text{ g}$	$74 \times 10^{-3} \text{ cm}^3$	$5476 \times 10^{-6} \text{ cm}^6$
ρ_a	$2.9 \times 10^4 \text{ cm}^6/\text{g}$	$0.29 \times 10^{-6} \text{ g/cm}^3$	$8 \times 10^{-3} \text{ cm}^3$	$64 \times 10^{-6} \text{ cm}^6$
ρ_h	$2.9 \times 10^4 \text{ cm}^6/\text{g}$	$0.02 \times 10^{-6} \text{ g/cm}^3$	$0.6 \times 10^{-3} \text{ cm}^3$	negligible
				$s^2(V_i) = 11016 \times 10^{-6} \text{ cm}^6$ $s(V_i) = 0.11 \text{ cm}^3$

The reaction is



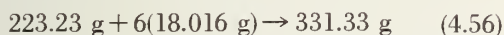
where $n=2, 4$, or 6 .

Under the dynamic conditions existing in the case of a flow of moist gas through the desiccant, it is possible for the reaction to yield all three hydrate forms.

The densities of the anhydrous and hexahydrate forms are given by Rossini [13] as 2.60 g/cm^3 and 1.970 g/cm^3 respectively. The density of the dihydrate form is given by Moles et al. [47] as 2.208 g/cm^3 .

Since there is a question as to the true final hydrate found in the tube and hence as to the volume change of the dessicant, it will be assumed that the actual volume change per gram of water absorbed lies midway between that obtained if the reaction yielded only the hexahydrate, and that obtained if it yielded only the dihydrate.

Substitution into eq (4.55) with $n=6$ leads to



so that 2.065 g of $\text{Mg}(\text{ClO}_4)_2$ combine with $1 \text{ g H}_2\text{O}$ to yield 3.065 g of hexahydrate.

The volume of the anhydrous form is $2.065/2.60 = 0.794 \text{ cm}^3$, while the volume of the hexahydrate is $3.065/1.970 = 1.556 \text{ cm}^3$. Thus for every gram of water absorbed, the desiccant volume increases by 0.762 cm^3 .

At the other extreme, if it is assumed that only the dihydrate is formed, it follows from eq (4.55) with $n=2$ that 6.195 g of $\text{Mg}(\text{ClO}_4)_2$ combine with 1 g of H_2O to yield 7.195 g of dihydrate. The volume of the anhydrous form is $6.195/2.60 = 2.383 \text{ cm}^3$ while the volume of the dihydrate is $7.195/2.208 = 3.259 \text{ cm}^3$. Thus in this case the desiccant volume changes 0.876 cm^3 for each gram of water absorbed.

If the true volume change per gram of water absorbed were midway between the two, then the desiccant volume would change 0.819 cm^3 per gram of water absorbed.

The uncertainty in the value of $0.819 \text{ cm}^3/\text{g}$ is at most $\pm 0.057 \text{ cm}^3/\text{g}$ for any run. This leads to a systematic uncertainty in the weighing accuracy.

The internal volume decrease is given by

$$v = x(W_f - W_i) \quad (4.57)$$

where $x = 0.819 \text{ cm}^3/\text{g}$, W_f is the final U-tube weight in g, and w_i the initial U-tube weight in g. The magnitude of v is 0.5 cm^3 .

Considering the difference $W_f - W_i$ to be a random variable, and applying error analysis to eq. 4.57 yields

$$s(v) = \left(\frac{\partial v}{\partial (W_f - W_i)} \right) s(W_f - W_i) \quad (4.58)$$

where

$$\frac{\partial v}{\partial (W_f - W_i)} = x. \quad (4.59)$$

Using the value $s(W_f - W_i) = 0.080 \text{ mg}$ (the experimental standard deviation of the weight gain of a single U-tube where handling is involved, given in sec. 4.2.j), it can be shown that $s(v) = 0.066 \text{ cm}^3$.

The amount of water absorbed by the second and third tubes, which contain P_2O_5 , is less than 0.2 mg . By performing a similar calculation where the end reaction product is assumed to be either HPO_3 or H_3PO_4 , it can be shown that the volume change from the small amount of water absorbed is negligible.

Error in Internal Gas Mass.—The random uncertainty in C_g may now be estimated by using eqs (4.45) through (4.48). The details of the computation are given in table 6. Nominal values of 30 cm^3 for V_f and V_i and of $1.17 \times 10^{-3} \text{ g/cm}^3$ for ρ_f and ρ_i were used. The standard deviation $s(C_g)$ so obtained is $8.5 \times 10^{-5} \text{ g}$.

g. Incompleteness of Water Vapor Absorption

Bower [32] has shown that the residual water vapor in a gas stream emerging from a U-tube filled with anhydrous $\text{Mg}(\text{ClO}_4)_2$ is $0.2 \times 10^{-3} \text{ mg/l}$, while Morley [33] has similarly demonstrated that an absorption tube packed with anhydrous P_2O_5 will remove all but $0.25 \times 10^{-4} \text{ mg/l}$ of water vapor from a gas stream at a flow rate of three liters per hour. The flow rate used in the gravimetric hygrometer may be as large as 2 lpm . Because of the large

TABLE 6. Standard deviation of the correction for mass of internal gas

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial C_g}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_g}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial C_g}{\partial z_n}\right)^2 s^2(z_n)$
V_i	10^{-4} g/cm^3	0.11 cm^3	$1.1 \times 10^{-5} \text{ g}$	$1.2 \times 10^{-10} \text{ g}^2$
v^*	$1.17 \times 10^{-3} \text{ g/cm}^3$	0.066	$7.7 \times 10^{-5} \text{ g}$	$59.3 \times 10^{-10} \text{ g}^2$
ρ_f	30 cm^3	$0.29 \times 10^{-6} \text{ g/cm}^3$	$9 \times 10^{-6} \text{ g}$	$0.8 \times 10^{-10} \text{ g}^2$
ρ_i	29.5 cm^3	$0.29 \times 10^{-6} \text{ g/cm}^3$	$9 \times 10^{-6} \text{ g}$	$0.8 \times 10^{-10} \text{ g}^2$

$$s^2(C_g) = 72.1 \times 10^{-10} \text{ g}^2$$

$$s(C_g) = 8.5 \times 10^{-5} \text{ g}$$

*In the case of the second and third tubes, the error in v has been shown to be negligible. For these tubes, it can be shown that $s(C_g) = 1.7 \times 10^{-5} \text{ g}$.

difference in flow between Morley's work and the present work, no correction will be made, and the systematic error in the weight of water arising from the incompleteness of absorption will be conservatively assigned a maximum value of $0.5 \times 10^{-4} \text{ mg}$ per liter of air collected.

h. Random Errors in the Measurement of Mass of Water Vapor

A numerical estimate will now be made for the random error involved in the measurement of the mass of water collected in a U-tube based on the uncertainties of the various independent parameters discussed above. The standard deviation $s(m)$ is given by eq (4.9). The individual sources of random error, the magnitude of their contributions, and the computed standard deviation $s(m)$ are summarized in table 7.

TABLE 7. Standard deviation of the mass of water collected in a U-tube*

Independent variable	Standard deviation	Variance
Z_n	$s(Z_n)$	$s^2(Z_n)$
W_f	$11 \times 10^{-6} \text{ g}$	$121 \times 10^{-12} \text{ g}^2$
W_i	$11 \times 10^{-6} \text{ g}$	$121 \times 10^{-12} \text{ g}^2$
C_w	$7.5 \times 10^{-6} \text{ g}$	$56 \times 10^{-12} \text{ g}^2$
C_b	$7.6 \times 10^{-6} \text{ g}$	$58 \times 10^{-12} \text{ g}^2$
C_a	Negligible	Negligible
C_g^{**}	$85 \times 10^{-6} \text{ g}$	$7225 \times 10^{-12} \text{ g}^2$

$$s^2(m) = 7581 \times 10^{-12} \text{ g}^2$$

$$s(m) = 87 \times 10^{-6} \text{ g}$$

*The error arising from the non-application of C_i is considered in the sec. on p. 29.

**Note that there is another case, where $s(C_g)$ is $1.7 \times 10^{-5} \text{ g}$ (see table 6). In that case it can be shown that $s(m) = 25 \times 10^{-6} \text{ g}$.

The standard deviation of the mass change of the first tube is $87 \times 10^{-6} \text{ g}$, and of the second and third tubes is $25 \times 10^{-6} \text{ g}$. The figure represents the error in mass gain in a tube where both the initial and final masses are each based on a single weighing. In practice, the U-tube is reweighed three times to obtain its initial mass and three times to obtain its final mass and the gain in mass is the difference between the initial and final average values.

From eq (4.4) it follows that for the latter case the standard deviation of the gain in mass for the first

tube is $87 \times 10^{-6} / \sqrt{3}$ or $50 \times 10^{-6} \text{ g}$, and for the second and third tube is $25 \times 10^{-6} / \sqrt{3}$ or $14 \times 10^{-6} \text{ g}$.

Since the first two tubes in the absorption train are used to compute the absorbed water in a run, then the standard deviation of the total mass of water collected is $[50 \times 10^{-6}]^2 + (14 \times 10^{-6})^2]^{1/2}$ or 0.052 mg .

i. Systematic Errors in the Mass of Water Vapor

There are two non-negligible systematic errors which must be considered. The first, arising from the differences in surface area of the U-tube and tare and the water vapor absorbed on these surfaces, was discussed in sec. 4.2.c. The maximum error expected from this effect was $\pm 4 \mu\text{g}$ per tube, and since two tubes are used for the water vapor mass determination, the maximum error for the water vapor mass determination is $\pm 8 \mu\text{g}$.

The other systematic error was discussed in the sec. on p. 17, where it was shown that the maximum uncertainty in the constant x of eq (4.57), important only for the first tube in the drying train, was $\pm 0.057 \text{ cm}^3/\text{g}$. Assuming that 0.6 g of water is absorbed in the first tube, it is seen that a maximum uncertainty of $\pm 0.034 \text{ cm}^3$ arises in the internal volume. Since the nominal air density in the tube is 1.17 mg/cm^3 , the systematic error in the mass of internal air and hence in the mass of water vapor collected may be as much as $\pm 0.04 \text{ mg}$.

The total possible systematic error in the mass of water vapor is therefore $0.04 + 0.008 = \pm 0.048 \text{ mg}$.

j. Blank Runs

Two types of experiments were performed to provide a check on the computed estimate of the error in the determination of the mass of water vapor absorbed by the main drying train. These experiments traced the degradation in accuracy of the weighing process with increasing complexity of the handling and manipulating operations.

The first experiment consisted of blank runs in which the actual conditions of a mixing ratio determination were simulated, except that air which had been successively pre-dried by $\text{Mg}(\text{ClO}_4)_2$ and P_2O_5 passed through the U-tubes. Each desiccant filled U-tube in this experiment was weighed, removed from the balance, stored, and subsequently inserted into the main drying train along with one or two other

filled U-tubes. Its stopcocks were opened, it was flushed with air from a high pressure cylinder that had been dried by passage through the flushing drying train at a flow rate of about 1.7 lpm, its stopcocks were closed, and it was reweighed.

The tube was weighed at least twice (generally three times or more) prior to a run, from which an average initial weight was computed. An identical procedure yielded an average final weight. The average final weight of one run was used as the initial average weight of the following run. Since the change in mass should be zero, the difference between the initial and final weight is a measure of the error. Three different U-tubes were used to form a total of fifteen runs. The results are shown in table 8.

TABLE 8. Dry runs: Estimate of the accuracy of the weight gain of a single tube

Tube No.	Run No.	Average U-tube weight* (mg×10 ²)	Difference in average weight (mg×10 ²)	(Difference) ²	Degrees of freedom
11		19			
	1	35	+ 16	256	
	2	25	- 10	100	
	3	30	+ 5	25	
	4	16	- 14	196	
	5	17	+ 1	1	
12	6	17	0	0	5
		19			
	7	23	+ 4	16	
	8	29	+ 6	36	
	9	34	+ 5	25	
	10	28	- 6	36	
14	11	23	- 5	25	
	12	21	- 2	4	5
		13			
	13	14	+ 1	1	
	14	8	- 6	36	
	15	9	+ 1	1	2

$$\Sigma(\text{Difference})^2 = 758 \quad \Sigma = 12$$

$$\text{Variance} = \frac{758}{12} = 63.2 \text{ mg}^2$$

$$\text{Standard Deviation} = 8.0 \times 10^{-2} \text{ mg}$$

*Only the final significant figures are given since only these changed from run to run.

The losses and gains in weight are almost equal in number and the sum of these is essentially zero. The blank runs did not disclose any systematic error. After applying a method for pooling data described by Youden [43] and assuming that these results may be extrapolated to actual mixing ratio determinations, it is estimated that the gain in mass in a single U-tube can be measured with a standard deviation of 0.080 mg and in two tubes, 0.113 mg.

Examination of the repeat U-tube weighings from which the initial and final average weights were calculated showed that the standard deviation of a single weighing was 0.044 mg. With 50 g and 100 g stainless steel weights a single mass determination could be made with a standard deviation of 0.011 mg (sec. 4.2a). If the latter value is considered to be indicative of the variability of the balance, then it appears that glass U-tubes are subject to effects that introduce additional errors in weighing. It is probable that dust accumulation,

static charge, moisture adsorption on external surfaces, convective currents within the balance case, and error in the buoyancy correction collectively contribute to this random error in weighing.

Based on a standard deviation of 0.044 mg for a single U-tube weight determination, the standard deviation of the difference between two weights, each the mean of n determinations, would be 0.044 $(2/n)^{1/2}$ (see sec. 4.1). For $n=3$, the standard deviation of the difference would be 0.036 mg, whereas the experimental result was 0.080 mg. It is apparent that manipulation during the dry flushings has introduced an additional random error.

A second experiment was performed in which a given mass of water was added to a stream of pre-dried air and was subsequently removed by the drying train. The water source was a U-tube containing about 1 g of distilled water through which the air passed at a rate of flow of approximately 1.5 lpm. The mass of water lost by the source was compared to the gain in mass by the first two tubes in the drying train. The third tube, in accordance with the practice adopted in this work, was used only as a guard tube.

TABLE 9. Moisture pick-up experiment

Run No.	Length of run (min)	Tube No.	Change in mass (a) g	Difference between the mass increase in the drying train and the mass decrease in the water source (e) mg × 10 ²	(Difference) ² mg ² × 10 ⁴
1	225	14(b)	+ 1.12445		
		11(c)	+ .00107		
			+ 1.12552		
2	225	15(d)	- 1.12532	+ 20	400
		14(b)	+ 1.09609		
		11(c)	+ .01721		
3	300		+ 1.11330		
		15(d)	- 1.11349	- 19	361
		14(b)	+ 1.15937		
4	296	11(c)	+ .01015		
			+ 1.16952		
		13(d)	- 1.16950	+ 2	4
5	490	J(b)	+ .74388		
		R(c)	+ .00011		
			+ .74399		
		A(d)	- .74407	- 8	64
		B(b)	+ 1.26387		
		J(c)	+ .00008		
			+ 1.26395		
		R(d)	- 1.26381	+ 14	196

$$\Sigma = 1025$$

$$\text{Variance} = 256 \text{ mg}^2 \times 10^4$$

$$\text{Standard Deviation} = 16 \text{ mg} \times 10^2$$

(a) Based on average of two to five weighings before and after the run.

(b) First tube in drying train.

(c) Second tube in drying train.

(d) Water source.

(e) Plus sign indicates drying train mass increase was greater than the water source mass decrease.

Each of the U-tubes, the one containing water, and the three in the drying train containing desiccant were weighed from two to five times before and after a run to provide average values for the initial and final weights. Five runs were made. The results are given in table 9. The differences between the mass increase in the drying train and the mass decrease in the water source show roughly equal numbers of plus and minus signs, indicating no pronounced tendency that could be ascribed to systematic effects. As in the previous experiment the differences will be assumed due to random errors. The standard deviation of a single determination of the difference between the water available and that gained is 0.16 mg. This is consistent with the results of the dry gas experiment which yielded 0.080 mg as the standard deviation for the mass determination of a single U-tube. Since three tubes were involved in each of the present runs (one tube with water and two tubes with desiccant), the predicted standard deviation of a run, based on 0.080 mg is $\sqrt{3} \times 0.080$ mg or 0.14 mg. Inversely, it could be stated that the final experiment yields a standard deviation of 0.092 mg for the mass determination by a single U-tube in the main drying train so that the standard deviation of the sum of the water vapor mass determinations by the first and second tubes is $\sqrt{2}(0.092) = 0.13$ mg. The standard deviation of the water vapor mass determination for any run therefore will be assumed to be 0.13 mg. Since this value is the larger of the calculated and experimental values and since it reflects handling errors in addition to those errors summarized in sec. 4.2.h, it will be used in subsequent calculations.

4.3. Measurement of the Gas Volume

The internal volumes of the two cylinders were measured by weighing each cylinder empty and then filled with distilled water. Each cylinder volume was computed using the equation

$$V_c = \frac{M}{d} - C_v \quad (4.60)$$

where

M = mass of water required to fill the cylinder at temperature t_c , g

d = density of water at temperature t_c and pressure B , g/cm³

V_c = volume at temperature t_c and pressure B , cm³

C_v = correction for water trapped in cylinder valves during filling operation, cm³.

Five independent determinations were made of each cylinder volume. Since the ambient conditions were not controlled, each determination involved a different temperature and barometric pressure. At atmospheric pressure, the change in cylinder volume (when filled with water) due to barometric fluctuations is negligible; the change because of temperature fluctuations, on the other

hand, is significant. Each experimental value of cylinder volume was therefore adjusted to the volume it would have at 25 °C, and these adjusted volumes were averaged to give a mean value.

Thus

$$V_0 = V_c + C_x \quad (4.61)$$

where

V_0 = volume at 25 °C and atmospheric pressure, cm³

C_x = correction for adjusting each experimentally determined volume to that of 25 °C.

The mean cylinder volume is

$$\bar{V}_0 = \frac{\sum V_0}{n} \quad (4.62)$$

where

$\sum V_0$ = sum of the experimentally determined and adjusted volumes, cm³.

n = number of experimental determinations.

The calibration results are given in table 10. Each cylinder has a volume capacity of about 29.7 liters at 25 °C.

TABLE 10. Internal volumes of cylinders at 25 °C

Run number	Cylinder no. 1		Cylinder no. 2	
	Volume, V_0 cm ³	Deviation from Mean, cm ³	Volume, V_0 cm ³	Deviation from Mean, cm ³
2	29658.8	-2.2	29734.2	-0.8
3	*29647.6		29732.9	-2.1
4	29654.0	-7.0	29736.6	+1.6
5	**29661.4	+0.4	29738.1	+3.1
6	29665.5	+4.5	29733.4	-1.6
7	29665.3	+4.3		
Mean	29661.0	±3.68	29735.0	±1.84
Standard deviation of the mean		2.15		0.99
Maximum		-7.0		+3.1

*Air trapped in cylinder. This value was not used to compute mean.

**Corrected for water trapped in vacuum exhaust valve.

In an actual run in which a moisture determination is being made, the cylinders may not be at the standard temperature of 25 °C. It will be necessary to adjust the mean cylinder volume to that of the test temperature by applying a correction whose magnitude will depend on the difference between these two temperatures, thus

$$V = \bar{V}_0 + C_t \quad (4.63)$$

where

V = volume at the cylinder test temperature, cm³

C_t = correction for adjusting the mean cylinder volume to that at the test temperature, cm³.

An analysis will now be made to obtain an estimate of the uncertainty in V_0 based on all known sources of error and this uncertainty will then be compared with the uncertainties derived from the experimental volume determinations shown in table 10. Finally, the uncertainty in determining V will be estimated.

a. Mass of Water

The mass of water required to fill a cylinder was determined by weighing the cylinder empty and then full using the substitution weighing method on a 50-kg balance. The accuracy of this mass determination is influenced by the variability of the balance, the calibration of the weights, and the correction for buoyancy of the cylinder and the weights. The mass of water was computed using the equation

$$M = W_f - W_i + C_w + C_b + C_r \quad (4.64)$$

where

M = mass of water, g

W_f = sum of face values of the weights used to achieve equilibrium with the filled cylinder, g

W_i = sum of face values of the weights used to achieve equilibrium with the empty open cylinder, g

C_w = sum of the corrections applied to the face values of the weights, g

C_b = buoyancy correction, g

C_r = correction for the inequality of balance armlengths, g.

Balance and Weights.—The variability of the 50-kg balance was assessed from the reciprocal sensitivity, with a given weight on both pans, and from the reproducibility of the rest point for that weight. With nominal loads on the pans of 30.5 kg and 60.1 kg, corresponding to the initial and final weights of a cylinder, the largest reciprocal sensitivities observed were 76 mg/div and 112 mg/div, and the greatest uncertainties in the rest point reproducibilities were 0.6 division and 0.8 division, respectively. Therefore, the maximum uncertainty arising from the nonreproducibility of the balance was 46 mg in W_i and 90 mg in W_f , so that the standard deviations were 15 mg and 30 mg, respectively.

The balance armlength ratio as experimentally determined by transposition weighing differs from unity by 2.5 ppm. This introduced a systematic error in the differential cylinder weight of $(W_f - W_i) \times 2.5 \times 10^{-6}$ g or 74 mg. A correction was made for this error, even though it was of small magnitude. The residual uncertainty was probably no greater than 1/2 ppm or 15 mg so that the standard deviation of C_r was 5 mg. The 1/2 ppm uncertainty contributes maximum errors of 30 mg and 15 mg in W_f and W_i , respectively.

The value for C_w was computed from the calibration corrections supplied by the NBS Mass Section for the specific set of class S weights [35] used, which, for weights of 10 g and above were deter-

mined with a maximum uncertainty of 3 ppm. Since $W_f - W_i$ was 29.6 kg, it follows that the maximum uncertainty in C_w was 89 mg and the standard deviation of C_w was 30 mg. Furthermore, the 3 ppm uncertainty contributes maximum uncertainties in the corrected values of W_f and W_i alone of 180 mg and 90 mg, respectively.

Buoyancy Correction.—Consider an equal arm balance with arm length L . Suspend a cylinder from the left arm and counterbalance it with weights suspended from the right arm. If X_i is the mass of the open and empty cylinder and W_i is the sum of the corrected weights required to bring the balance into equilibrium then

$$X_i L - X_i \frac{\rho_i}{\rho_x} L = W_i L - W_i \frac{\rho_i}{\rho_w} L \quad (4.65)$$

or

$$X_i = W_i \frac{1 - \frac{\rho_i}{\rho_w}}{1 - \frac{\rho_i}{\rho_x}} \quad (4.66)$$

where

ρ_i = density of the air at the time of the weighing of the empty cylinder, g/cm³

ρ_x = density of the open and empty cylinder, g/cm³

ρ_w = density of the weights, g/cm³.

Neglecting all third and higher order terms, the empty cylinder mass is

$$X_i = W_i \left[1 - \frac{\rho_i}{\rho_w} + \frac{\rho_i}{\rho_x} - \frac{\rho_i^2}{\rho_x \rho_w} + \frac{\rho_i^2}{\rho_x^2} \right] \quad (4.67)$$

If X_f is the mass of the closed and filled cylinder, W_f the sum of the corrected weights required to bring the balance into equilibrium, ρ_f the air density at the time of the weighing of the filled cylinder, and ρ_{H_2O} the density of the water in the cylinder, then, neglecting all third and higher order terms,

$$X_f = W_f - W_f \frac{\rho_f}{\rho_w} + W_i \left[\frac{\rho_f}{\rho_x} - \frac{\rho_f}{\rho_x} \frac{\rho_i}{\rho_w} + \frac{\rho_f}{\rho_x} \frac{\rho_i}{\rho_x} \right] + (X_f - X_i) \frac{\rho_f}{\rho_{H_2O}} \quad (4.68)$$

The mass of water in the cylinder, again neglecting third and higher order terms is

$$\begin{aligned} (X_f - X_i) = & (W_f - W_i) \left[1 + \frac{\rho_f}{\rho_{H_2O}} + \frac{\rho_f^2}{\rho_{H_2O}^2} \right] \\ & - W_f \left[\frac{\rho_f}{\rho_w} + \frac{\rho_f^2}{\rho_w \rho_{H_2O}} \right] + W_i \left[\frac{\rho_f}{\rho_x} + \frac{\rho_i}{\rho_w} - \frac{\rho_i}{\rho_x} \right. \\ & - \frac{\rho_f \rho_i}{\rho_x \rho_w} + \frac{\rho_f \rho_i}{\rho_x^2} + \frac{\rho_i^2}{\rho_x \rho_w} - \frac{\rho_i^2}{\rho_x^2} \\ & \left. + \frac{\rho_f^2}{\rho_x \rho_{H_2O}} + \frac{\rho_i \rho_f}{\rho_w \rho_{H_2O}} - \frac{\rho_i \rho_f}{\rho_x \rho_{H_2O}} \right]. \quad (4.69) \end{aligned}$$

TABLE 11. Standard deviation of the buoyancy correction in the cylinder volume determination

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial C_b}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right)^2 s^2(z_n)$
ρ_i	280 cm ³	0.42×10^{-6} g/cm ³	0.000 g	0.000000 g ²
ρ_f	26420 cm ³	0.42×10^{-6} g/cm ³	0.011 g	0.000121 g ²
ρ_{H_2O}	34.5 cm ³	45×10^{-6} g/cm ³	0.002 g	0.000004 g ²
W_f	1.00103	0.050 g	0.050 g	0.002500 g ²
W_i	1.00964	0.100 g	0.101 g	0.010201 g ²

$$s^2(C_b) = 0.012826 \text{ g}^2$$

$$s(C_b) = 0.113 \text{ g}$$

It can be shown that the magnitudes of the second order terms are of the order of 40 mg or less and that they tend to cancel or compensate. Eq (4.69) therefore may be reduced to

$$(X_f - X_i) = (W_f - W_i) \left[1 + \frac{\rho_f}{\rho_{H_2O}} \right] - W_f \frac{\rho_f}{\rho_w} + W_i \left[\frac{\rho_f}{\rho_x} + \frac{\rho_i}{\rho_w} - \frac{\rho_i}{\rho_x} \right] \quad (4.70)$$

or

$$(X_f - X_i) = (W_f - W_i) + C_b \quad (4.71)$$

where C_b is the buoyancy correction and given by

$$C_b = (W_f - W_i) \frac{\rho_f}{\rho_{H_2O}} - W_f \frac{\rho_f}{\rho_w} + W_i \left[\frac{\rho_f}{\rho_x} + \frac{\rho_i}{\rho_w} - \frac{\rho_i}{\rho_x} \right] \quad (4.72)$$

The magnitude of C_b is about 31 g. Consider now the errors involved in computing C_b .

The air density was calculated using eq (4.23). The estimate of uncertainty in the air density is the same as that given in the sec. on p. 12, that is, $s(\rho_i) = s(\rho_f) = 0.42 \times 10^{-6}$ g/cm³. Similarly, the considerations given in this same section regarding the variables ρ_w and ρ_{H_2O} apply.

The estimate of the uncertainty in the water density is $s(\rho_{H_2O}) = 45 \times 10^{-6}$ g/cm³. The error in the assumed density of the weights may be as large as ± 0.1 g/cm³, giving rise to a systematic error in C_b of ± 0.06 g.

The cylinders and the attached valves were fabricated from stainless steel which has a nominal density of 7.8 g/cm³. However, attached to the cylinders were a few small brass fittings used in the filling operation and coupled to the valves were aluminum air actuators. The uncertainty in the nominal density is systematic and may be as great as ± 0.2 g/cm³ leading to a maximum contribution to the buoyancy error of ± 0.001 g.

The sources of the uncertainties in W_i and W_f were discussed in the preceding section. The maximum uncertainties for W_i due to the balance variability, the calibration error, and the inequality of arms were 46, 90, and 15 mg for a total of 151 mg; for W_f the corresponding contributions were 90, 180, and 30 mg for a total of 300 mg. The standard devia-

tions will be assumed to be $s(W_i) = 50$ mg and $s(W_f) = 100$ mg.

The following nominal values were utilized in calculating the numerical values of the partial derivatives. $W_i = 30.55$ kg, $W_f = 60.13$ kg, $\rho_i = \rho_f = 1.161 \times 10^{-3}$ g/cm³, $\rho_{H_2O} = 0.997$ g/cm³, $\rho_w = 8.4$ g/cm³, $\rho_x = 7.8$ g/cm³, $\rho_f - \rho_i = 10^{-5}$ g/cm³.

The steps in the computation of the uncertainty in C_b due to random effects are given in table 11. The estimate for the standard deviation $s(C_b)$ is 0.113 g.

Error in the Mass Determination.—The random uncertainty in the mass determination is computed from the equation

$$s(M) = [s^2(W_f) + s^2(W_i) + s^2(C_w) + s^2(C_r) + s^2(C_b)]^{1/2} \quad (4.73)$$

Note that in this case, W_f and W_i are the uncorrected values (as opposed to the case in eq 4.72), and their errors depend only on the balance variability and arm ratio errors, which are discussed in the sec. on p. 21. The maximum errors from these sources are 120 mg in W_f and 61 mg in W_i , leading to the respective standard deviations of 40 mg and 20 mg.

The calculations in table 12 show that $s(M) = 0.125$ g.

TABLE 12. Standard deviation of the mass of water used in the cylinder calibration

Independent variable	Standard deviation	Variance
z_n	$s(z_n)$	$s^2(z_n)$
W_f	0.040 g	0.001600 g ²
W_i	0.020 g	0.000400 g ²
C_w	0.030 g	0.000900 g ²
C_r	0.005 g	0.000025 g ²
C_b	0.113 g	0.012770 g ²

$$s^2(M) = 0.015695 \text{ g}^2$$

$$s(M) = 0.125 \text{ g}$$

b. Water Density

The sources of error in the density of the water used in the cylinder volume determination are the same as those discussed in the sec. on p. 12. The same value for the standard deviation of the density estimated there will be used here, that is, 45×10^{-6} g/cm³.

c. Cylinder Valve Correction

The cylinder volume is that volume enclosed by the shut inlet valve, barometer valve, and vacuum gage valve. In filling the cylinder with water for calibration a procedure was followed whereby water was unavoidably or inadvertently trapped in one or more of the valves. This trapped water, which filled the channel in the ball of the valve was, of course, weighed. A volumetric correction, based on the geometry of the channel, was therefore made to reduce this systematic error. This correction was computed by the equation

$$C_v = \frac{\pi D^2}{4} \times L_c \quad (4.74)$$

where D is the diameter of the cylindrical channel and L_c is the length of the channel. Since D is 3/8 in. and $L_c = 3/4$ in. for the 1/4-in. valve (water was not trapped in the large valve), C_v is 1.36 cm³.

The maximum uncertainty ΔC_v is estimated from the equation

$$\Delta C_v = \frac{\partial C_v}{\partial D} \Delta D + \frac{\partial C_v}{\partial L_c} \Delta L_c \quad (4.75)$$

where

$$\frac{\partial C_v}{\partial D} = \frac{\pi D L_c}{2} \quad (4.76)$$

$$\frac{\partial C_v}{\partial L_c} = \frac{\pi D^2}{4} \quad (4.77)$$

ΔD = maximum uncertainty in D

ΔL_c = maximum uncertainty in L_c .

Normal engineering tolerances permit a maximum error of $\pm 1/64$ in. in any dimension, unless otherwise specified. In the absence of any direct measurements of D or L_c , it will be assumed that the maximum uncertainty in each is $\pm 1/64$ in. from which it follows that ΔC_v for a single valve is ± 0.14 cm³ and for three valves, ± 0.42 cm³. This error is systematic.

An estimate is made of the random uncertainty in V_c by applying eqs (4.2) and (4.3) to (4.60). A nominal water density of 1 g/cm³ is used. The standard deviation $s(V_c)$, as indicated in table 13, is 1.34 cm³.

d. Correction to a Standard Temperature

The following correction was applied to each experimentally determined cylinder volume in order to adjust it to the value it would have at the standard temperature of 25 °C:

$$C_x = V_c \alpha (t_o - t_e) \quad (4.78)$$

where

C_x = correction, cm³

α = coefficient of volumetric expansion for the cylinder, cm³/cm³/°C

t_o = standard temperature, i.e., 25 °C

t_e = temperature at which volume V was determined, °C

V_c = volume of cylinder at temperature t_e , cm³.

The cylinder is fabricated from type 316 stainless steel. Interpretations of the data of Furman [48], Beenaker and Swenson [49], Lucks and Deem [50], and the Metals Handbook [51] lead to values of the coefficient of linear expansion of 316 stainless steel of 15.2, 15.6, 15.3, and 15.8, all in units of 10^{-6} cm/cm/°C. If all these values are given equal weight, the mean is 15.48×10^{-6} cm/cm/°C. Assuming that the coefficient of volumetric expansion is three times the coefficient of linear expansion, then the mean $\alpha = 46.4 \times 10^{-6}$ cm³/cm³/°C with a standard deviation of the mean of 0.45×10^{-6} cm³/cm³/°C. The correction per deg C, that is, $V_c \alpha$, is 29700 cm³ $\times 46.4 \times 10^{-6}$ cm³/cm³/°C or 1.38 cm³/°C where 29700 cm³ is the nominal cylinder volume.

The terms contributing to the uncertainty in C_x are found by applying (4.2) and (4.3) to (4.78).

The following nominal values of the parameters were used in the calculations:

$$\begin{aligned} \alpha &= 46.4 \times 10^{-6} \text{ cm}^3/\text{cm}^3/^\circ\text{C}, \\ V_c &= 29700 \text{ cm}^3, \\ (t_o - t_e) &= 2^\circ\text{C}. \end{aligned}$$

The computations and results are shown in table 14. The standard deviation $s(C_x)$ is 0.14 cm³.

e. Random Error in the Measurement of Gas Volume

The estimated standard deviation of the volume adjusted to 25 °C, $s(V_0)$, is given by $[s(V_c)^2 + s(C_x)^2]^{1/2}$

TABLE 13. Standard deviation of the cylinder volume at the calibration temperature

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial V_c}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_c}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial V_c}{\partial z_n}\right)^2 s^2(z_n)$
M	1 cm ³ /g	0.125 g	0.125 cm ³	0.0157 cm ⁶
d	29.6×10^3 g	45×10^{-6} g/cm ³	1.33 cm ³	1.77 cm ⁶

$$\begin{aligned} s^2(V_c) &= 1.79 \text{ cm}^6 \\ s(V_c) &= 1.34 \text{ cm}^3 \end{aligned}$$

TABLE 14. *Standard deviation of the cylinder volume correction to a standard temperature*

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial C_x}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_x}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial C_x}{\partial z_n}\right)^2 s^2(z_n)$
V_c	$93 \times 10^{-6} \text{ cm}^3/\text{cm}^3$	1.34 cm^3	0.000 cm^3	0.0000 cm^6
α	$59.4 \times 10^3 \text{ cm}^3/\text{deg C}$	$0.45 \times 10^{-6} \text{ cm}^3/\text{cm}^3/\text{deg C}$	0.027 cm^3	0.0007 cm^6
t_c	$1.38 \text{ cm}^3/\text{deg C}$	$0.1 \text{ }^\circ\text{C}$	0.138 cm^3	0.0190 cm^6

$$s^2(C_x) = 0.0197 \text{ cm}^6$$

$$s(C_x) = 0.14 \text{ cm}^3$$

or 1.35 cm^3 . The estimated standard deviation of the mean volume $s(\bar{V}_0)$, based on n repeated determinations of V_0 , is $s(V_0)/\sqrt{n}$ which reduces to 0.60 cm^3 for $n=5$. The experimental standard deviations of the mean volume determinations were 2.15 cm^3 and 0.99 cm^3 for cylinder nos. 1 and 2 respectively (table 10). It is apparent that the estimate of the uncertainty in the volume determination based on an error analysis yields a value that is of the same order of magnitude as the experimental uncertainty.

If the gas volume measuring system, during a moisture determination, is maintained at some temperature other than $25 \text{ }^\circ\text{C}$, then the mean volumes, listed in table 10, must be adjusted to the test temperature t by adding or subtracting the correction

$$C_t = \bar{V}_0 \alpha (t - 25^\circ) \quad (4.79)$$

as indicated in eq (4.63).

The uncertainty in C_t per deg C difference between t and $25 \text{ }^\circ\text{C}$ may be evaluated by applying eqs (4.2) and (4.3) to (4.79). The nominal values used for α and V are those given in sec. 4.3.d. Letting $t - 25^\circ$ be equal to $1 \text{ }^\circ\text{C}$, a calculation similar to that given in sec. 4.3.d may be made, the only additional difference being that the standard deviation of t , based on considerations given in sec. 4.4.c, is $0.009 \text{ }^\circ\text{C}$.

It follows that for each $^\circ\text{C}$ difference between t and t_0 , the standard deviation of C_t is 0.02 cm^3 and therefore

$$s(V) = \left[s(\bar{V}_0)^2 + 0.0004(t - 25^\circ)^2 \right]^{1/2} \quad (4.80)$$

f. Systematic Errors in the Gas Volume

The non-negligible systematic errors in the cylinder volumes and thus in the gas volumes arise in the buoyancy correction (see sec. on p. 21) and the cylinder valve correction (sec. 4.3.c).

The former leads to a maximum uncertainty in C_b and thus in the water mass of $\pm 0.06 \text{ g}$. This corresponds to a maximum uncertainty in the cylinder volume of $\pm 0.06 \text{ cm}^3$.

The latter, arising from the cylinder valve connection, led to a maximum uncertainty in the cylinder volume of $\pm 0.42 \text{ cm}^3$.

Altogether there is a maximum possible systematic error in the cylinder volume of $\pm 0.48 \text{ cm}^3$.

4.4. Determination of the Gas Density in a Cylinder

The gas of principal interest in humidity measurement is atmospheric air; hence, the discussion and error analysis will be confined to this gas although similar analyses may be made for other gases.

a. Standard Density

Air is primarily a mixture of oxygen, nitrogen, argon, and carbon dioxide. The percentage composition of the components is essentially constant. Such variables as geographic location, altitude, and presence of sources of contamination have little detectable effect on the percentage composition [52, 53]. The percentages and their standard deviations, as given by Gluekauf [53] are as follows: Nitrogen—78.084 ($s=0.004\%$), oxygen—20.946 ($s=0.002\%$), carbon dioxide—0.033 ($s=0.001\%$), and argon—0.934 ($s=0.001\%$). However, the CO_2 content is apparently increasing [52, 53], and the above standard deviations are for the year 1950. Therefore a standard deviation of 0.004 percent will be used instead of 0.001 percent for CO_2 .

The value of ρ_0 , the density of air at $273.16 \text{ }^\circ\text{K}$ and 760 mm Hg , is computed from the equation

$$\rho_0 = \frac{M_a}{V_a} = \frac{M_a}{Z_0 V} \quad (4.81)$$

where M_a is the molecular weight of air in grams/mole, and V_a is the molar volume in cm^3/mole that air occupies under standard conditions. Since air is not an ideal gas, V_a is equal to V , the molar volume an ideal gas occupies under standard conditions, multiplied by Z_0 , the compressibility factor for air at $273.16 \text{ }^\circ\text{K}$ and 760 mm Hg .

The molecular weight of air is given by

$$M_a = \%N_2(M_{N_2}) + \%O_2(M_{O_2}) + \%CO_2(M_{CO_2}) + A(M_A) \quad (4.82)$$

where the M 's and their corresponding subscripts denote the molecular weights of the four components listed above.

Therefore ρ_0 is given by

$$\rho_0 = \frac{\%N_2(M_{N_2}) + \%O_2(M_{O_2}) + \%CO_2(M_{CO_2}) + \%A(M_A)}{V Z_0} \quad (4.83)$$

TABLE 15. Standard deviation of ρ_0

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial \rho_0}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho_0}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho_0}{\partial z_n}\right)^2 s^2(z_n)$
%N ₂	$1.25064 \times 10^{-3} \text{ g/cm}^3$	0.00004	$5.0026 \times 10^{-8} \text{ g/cm}^3$	$25.026 \times 10^{-16} \text{ g}^2/\text{cm}^6$
%O ₂	$1.42848 \times 10^{-3} \text{ g/cm}^3$	0.00002	$2.8570 \times 10^{-8} \text{ g/cm}^3$	$8.162 \times 10^{-16} \text{ g}^2/\text{cm}^6$
%CO ₂	$1.96465 \times 10^{-3} \text{ g/cm}^3$	0.00004	$7.8586 \times 10^{-8} \text{ g/cm}^3$	$61.758 \times 10^{-16} \text{ g}^2/\text{cm}^6$
%A	$1.78533 \times 10^{-3} \text{ g/cm}^3$	0.00001	$1.7853 \times 10^{-8} \text{ g/cm}^3$	$3.187 \times 10^{-16} \text{ g}^2/\text{cm}^6$
M_a	$2.678 \times 10^{-8} \text{ l/cm}^3$	$6 \times 10^{-4} \text{ g}$	$16.0680 \times 10^{-12} \text{ g/cm}^3$	Negligible
V	$5.769 \times 10^{-8} \text{ g/cm}^6$	0.9 cm^6	$5.1921 \times 10^{-8} \text{ g/cm}^2$	$26.958 \times 10^{-16} \text{ g}^2/\text{cm}^6$

$$s^2(\rho_0) = 0.0125 \times 10^{-12} \text{ g}^2/\text{cm}^6$$

$$s(\rho_0) = 0.1 \times 10^{-6} \text{ g/cm}^3$$

Using the above percentages for the components and the following values for their molecular weights, N₂=28.016 g/mole, O₂=32 g/mole, CO₂=44.011 g/mole, and A=39.944 g/mole, and using $V = 22414.6 \text{ cm}^3$ [54] and $Z_0 = 0.99941$ [36], it is found that $\rho_0 = 1.29304 \times 10^{-3} \text{ g/cm}^3$.

The fact that there are uncertainties in ρ arising from uncertainties in composition will be taken into account by letting these uncertainties contribute to the standard deviation of ρ_0 .

Using eqs (4.83) and (4.3), the terms contributing to the standard deviation of ρ_0 are found.

According to information available at the National Bureau of Standards [55], the contribution of the maximum uncertainties in the molecular weights of the constituents to the maximum uncertainty of the molecular weight of air is 4 or 5 parts in 10^5 from nitrogen, and a maximum of 1 part in 10^5 for the remaining components. This gives a total maximum uncertainty of 6 parts per 10^5 . Applying the 3 sigma rule, the standard deviation of the molecular weight of air is 2 parts in 10^5 . The molecular weight of air is 28.966 g/mole as computed from eq (4.83). Therefore its standard deviation is $6 \times 10^{-4} \text{ g/mole}$.

The standard deviation of V is 0.9 cm^3 [54].

According to Hilsenrath [36], the uncertainty in Z_0 is nominally zero.

From the computations in table 15, the standard deviation of ρ_0 is $0.1 \times 10^{-6} \text{ g/cm}^3$.

The density of air at any other temperature T and pressure B is given by

$$\rho = \rho_0 \times \frac{273.16}{T} \times \frac{B}{760} \times \frac{Z_0}{Z} \quad (4.84)$$

where Z , the compressibility factor, is a function of T and B .

Hilsenrath [36] has shown that the differences between compressibility factors of his tables and the tables obtained by other researchers, at a nominal pressure of 1 atm, is zero at 273.16 °K and 1 part in 10^4 at 323.16 °K. If this is interpolated linearly, the difference increases 2 parts in 10^6 per deg K. Therefore at 300 °K, the difference is 5.4 parts in 10^5 . This will be taken as the standard deviation of the compressibility factor for the present purpose.

The compressibility factor at one atmosphere and 300 °K is nominally unity, so its standard deviation is 54×10^{-6} .

b. Pressure

The accuracy with which the pressure in a cylinder can be measured depends on the barometer errors, the residual gas pressure at the cessation of evacuation, the fluctuations at the assumed equilibrium point, leakage in the barometer system, and the error due to the difference between the pressure in the barometer system and that in the cylinder at the moment the barometer valve is opened.

A precision micrometer cistern mercury barometer is used to measure the equilibrium pressure within a cylinder. This instrument was calibrated by the NBS Pressure and Vacuum Section in the latter part of 1960. After applying corrections for the zero reading, capillary depression, temperature, and gravity, it is estimated that the standard deviation of a pressure measurement, arising from the barometer itself, is 0.08 mm Hg.

The barometer scale was independently calibrated with gage blocks, with another mercury manometer, and with a piston gage. At 20 °C and 700 mm Hg, the gage block calibration indicates a scale correction of -0.005 mm Hg , whereas both of the other methods indicate nominal scale corrections of $+0.120 \text{ mm Hg}$.

Because of this discrepancy, a correction of $+0.065 \text{ mm Hg}$ will be applied to any reading, and a residual systematic error of $\pm 0.075 \text{ mm Hg}$ will be assigned to any reading.

The equilibrium values of the pressures in a given cylinder with repeated evacuation and filling have varied as much as 1.3 mm Hg, although a more typical value would be 0.5 mm Hg. The variations arise from the photocell circuit response time and the variability of the flow rate at this part of the cycle. Because of the magnitude of the variations, the actual pressure must be recorded each time equilibrium has been reached.

Fluctuations also occur after the cylinder has presumably attained equilibrium. Since it is not known whether these fluctuations arise from the nonreproducibility of the barometer or are real fluctuations, the latter will be assumed, in which

case this contributes another uncertainty to the pressure. The largest such fluctuation has been about 0.2 mm Hg, although the more usual figure is 0.025 mm Hg. The standard deviation will be assumed to be represented by 1/3 of the maximum, that is, 0.07 mm Hg.

The total standard deviation of a single pressure reading, because of errors in the barometer itself and the fluctuations which occur is given by

$$s(p) = \left[(0.08)^2 + (0.07)^2 \right]^{1/2} \quad (4.85)$$

or

$$s(p) \approx 0.10 \text{ mm Hg.}$$

At least three barometer readings are taken after the cylinder has reached its equilibrium pressure, and these are averaged. The standard deviation of the average pressure within a cylinder is thus given by

$$\frac{s(p)}{\sqrt{3}} = 0.06 \text{ mm Hg.} \quad (4.86)$$

The barometer system (that is, the cistern and connecting tubing) is not necessarily at the equilibrium pressure of the cylinders before a run is started. As a result, air from the system is dumped into a cylinder, or vice versa (depending on which is initially greater), resulting in a pressure reading that depends both on the true cylinder pressure, and on the pressure in the barometer system before connection to the cylinder. The excess air is shunted back and forth between cylinders as they open and close, so that the correction need only be applied once, upon completion of the run.

The correction is of the form

$$P_c = \frac{V_s \Delta P + A(P_f^2 - P_i^2)}{V_c} \quad (4.87)$$

where

V_s = barometer system volume when column and cistern are at same pressure, cm^3

P_f = final cylinder pressure reading on barometer, cm

P_i = initial pressure reading on barometer before run begins, cm

$\Delta P = P_f - P_i$, cm

A = area of barometer column, cm^2

V_c = volume of cylinder to which the barometer is finally connected, cm^3 .

The same correction applies for the pressure switch, although for it P_f and P_i represent final and initial ambient pressures. The sum of the two corrections is about 0.1 mm Hg.

The residual errors, after applying the correction to both systems, are estimated to be one part in 40,000 if the pressure reading is 100 mm Hg or greater, that is, when a cylinder has collected 1/7 of its volume, or nominally 4.2 liters.

The leak rate of the barometer system is such that the mercury column moves 0.006 mm/min under a vacuum of less than 100μ Hg.

The length of time the barometer system is open to a cylinder is roughly 10 min, the latter half of which is under equilibrium conditions. If the leak rate were 0.006 mm/min at the equilibrium pressure of 695 mm Hg, the column would be expected to move upward 0.03 mm Hg during the reading time. This is not observed, indicating that error from the leak rate at the equilibrium pressure is negligible.

Each cylinder was repeatedly evacuated to determine its residual pressure just prior to filling. These tests showed that each cylinder reached 50μ Hg in about 93 sec.

At the time of the momentary closing and reopening of the vacuum valve of the cylinder being evacuated, i.e., 120 sec after the start of evacuation (see sec. 7), the cylinder pressure was about 37μ Hg. The closing and reopening of the valve caused the cylinder pressure to rise again to approximately 75μ Hg after which it returned to the value it had had prior to the closing in approximately 90 sec.

At the maximum flow rate of 2 lpm of air into one cylinder, the other cylinder was evacuated for about 420 sec, at which time the pressure in that cylinder was reduced to about 23μ .

Both cylinders had residual pressures of less than 20μ Hg after evacuation for 600 sec, and after 2100 sec the pressures had decreased to 17μ Hg.

The residual back pressure within the cylinder when it is opened for filling after evacuation, as measured with the system's thermocouple vacuum gage, is no greater than 20μ Hg. This is a systematic error for which a correction may be applied. However, the magnitude of this error, about 1 part in 35,000, is so small that it may be neglected. The scatter of the observations after repeated evacuations is about 10μ Hg, which is only 1 part in 70,000 of the equilibrium pressure of 695 mm Hg and thus negligible. Therefore the only random factor contributing to the accuracy of the cylinder pressure that is significant is the barometer error which is 0.06 mm Hg.

c. Temperature

The uncertainties in the temperature measurement of the gas in the cylinder arise from the error in the thermopile calibration, the accuracy of the potentiometer used for measuring the thermopile voltage, and the fluctuations about the mean equilibrium temperature.

Each thermopile was calibrated at nominal temperatures of 20° , 25° , 30° , and 35° C against a NBS calibrated platinum resistance thermometer for which the estimated maximum error is 0.001 deg C. The thermopile has an output of about 160 microvolts per deg C; the potentiometer used to measure this output has a maximum uncertainty of 1 microvolt; therefore, the calibration data had an equivalent

maximum uncertainty of 0.006 deg C. In order to permit interpolation between thermopile calibration points, the data were fitted to an empirical equation of the form

$$E = at + bt^2 + ct^3 + dt^4 \quad (4.88)$$

This equation was used to compute the emf outputs for temperatures at 1/2 deg C intervals and straight lines were then drawn between successive points. These lines are used to convert emf readings into temperature. A comparison of interpolated values, as derived from the curves and the experimental data disclosed that the maximum difference was 0.011 deg C. Subsequent to the calibration, each measurement with the thermopile involves the use of the potentiometer so that the latter again contributes an uncertainty of 0.006 deg C.

During each cycle of evacuation and filling, the gas within a cylinder undergoes an adiabatic expansion and compression with an accompanying decrease in temperature, followed by an increase in temperature and a final leveling off in temperature at an equilibrium value. Figure 5 shows typical temperature variations within the cylinders and the surrounding oil bath during a 4-hour period when the bath was closely regulated at a nominal control temperature of 29 °C. The bath temperature fluctuated over a range of 0.007 deg C for time intervals of 1.5 to 3 min between maximum and minimum values. Over the 4-hour test period, the overall

spread of the bath temperature was 0.016 deg C. The temperature first decreased, then it increased to within 0.003 deg C of its previous highest value. Thus, the bath temperature showed short time variations superimposed on a long time overall drift, but did not vary more than 0.016 deg C during the 4-hour period.

The equilibrium temperature of both cylinders (after filling) was found to be slightly lower than the bath temperature (approximately 0.033 deg C lower in cylinder no. 1 and 0.015 deg C lower in cylinder no. 2). The systematic differences in the equilibrium temperatures of the cylinders and the bath is ascribed to circulation patterns established within the bath. When the vacuum exhaust valve of either cylinder was opened, the temperature within that cylinder dropped in less than 1/2 min approximately 0.9 deg C, then in the next two minutes increased about 0.45 °C and finally attained a temperature when the vacuum valve closed that was about 0.02 deg C less than the equilibrium temperature. As each cylinder filled (at an average rate of 1 lpm, in these tests), the temperature increased monotonically, rising approximately 0.33 deg C above the bath temperature before the inlet valve closed. Upon closing of the inlet valve, the temperature dropped 0.16 deg C in 30 sec, and finally reached equilibrium in less than 12 minutes. Although the total adiabatic temperature change was of the order of 1.25 deg C, there was adequate time for the air within a filled cylinder to reach temperature equilibrium.

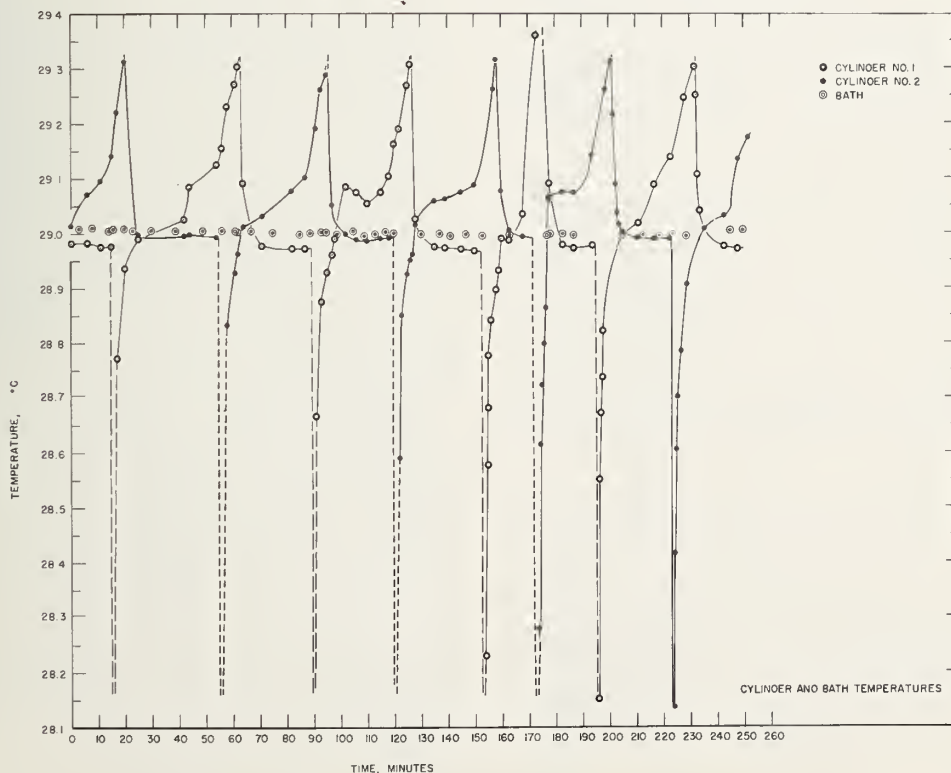


FIGURE 5. Bath and cylinder temperatures during cycling.

TABLE 16. Standard deviation of the density of air in a cylinder

Independent variable	Partial derivative	Standard deviation		Variance
z_n	$\frac{\partial \rho}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right)^2 s^2(z_n)$
Z	$1.09 \times 10^{-3} \text{ g/cm}^3$	54×10^{-6}	$58.9 \times 10^{-9} \text{ g/cm}^3$	$0.0035 \times 10^{-12} \text{ g}^2/\text{cm}^6$
ρ_0	0.844	$0.1 \times 10^{-6} \text{ g/cm}^3$	$0.0844 \times 10^{-6} \text{ g/cm}^3$	$0.0071 \times 10^{-12} \text{ g}^2/\text{cm}^6$
T	$3.67 \times 10^{-6} \text{ g/cm}^3 \text{ }^\circ\text{K}$	0.008 $^\circ\text{K}$	$0.029 \times 10^{-6} \text{ g/cm}^3$	$0.0008 \times 10^{-12} \text{ g}^2/\text{cm}^6$
B	$1.57 \times 10^{-6} \text{ g/cm}^3 \text{ mm Hg}$	0.06 mm Hg	$0.09 \times 10^{-6} \text{ g/cm}^3$	$0.0081 \times 10^{-12} \text{ g}^2/\text{cm}^6$

$$s^2(\rho) = 0.0195 \times 10^{-12} \text{ g}^2/\text{cm}^6$$

$$s(\rho) = 0.14 \times 10^{-6} \text{ g/cm}^3$$

The equilibrium temperature fluctuated about 0.002 deg C. Since it is not known whether this is because of the nonreproducibility of the thermopiles or whether it is real, an error of this magnitude will be assigned to the temperature.

The sum of the uncertainties in the measurement of cylinder temperature is thus 0.026 $^\circ\text{C}$. It will be assumed, therefore, that the standard deviation of the gas temperature in the cylinder at equilibrium is 0.009 deg C, that is 1/3 of the maximum uncertainty (see sec. 4.1).

d. Random Error in the Determination of Gas Density

Substitution of the appropriate partial derivatives of eq (4.84) into eq (4.3), along with the required standard deviations, leads to the terms contributing to the uncertainty in the gas density. The nominal values used for the independent parameters are $\rho_0 = 1.3 \times 10^{-3} \text{ g/cm}^3$, $Z_0/Z = 1$, $T = 298 \text{ }^\circ\text{K}$, and $B = 700 \text{ mm Hg}$. As indicated in table 16, $s(\rho) = 0.14 \times 10^{-6} \text{ g/cm}^3$. This value varies slightly with temperature, but the variations are insignificant for the present purpose.

e. Systematic Error in the Determination of Gas Density

The only nonnegligible systematic error occurring in this determination is that arising from the uncertainty of the scale correction to the barometer. As mentioned in sec. 4.4.b, the magnitude of this error is $\pm 0.075 \text{ mm Hg}$.

Use of the density eq (4.23) shows that the magnitude of the corresponding systematic error in the air density is $\pm 0.12 \times 10^{-6} \text{ g/cm}^3$.

4.5. Accuracy in the Determination of Mixing Ratio

a. Random Error in the Mixing Ratio

The mixing ratio is defined by eq (1.1) while the standard deviation of the mixing ratio is given by eq (4.6). The latter equation is repeated here.

$$s(r) = \left[\left(\frac{\partial r}{\partial M} \right)^2 s^2(M) + \left(\frac{\partial r}{\partial V} \right)^2 s^2(V) + \left(\frac{\partial r}{\partial \rho} \right)^2 s^2(\rho) \right]^{1/2} \quad (4.89)$$

where

$$\frac{\partial r}{\partial M} = \frac{1}{V\rho} \quad (4.90)$$

$$\frac{\partial r}{\partial V} = -\frac{M}{V^2\rho} \quad (4.91)$$

$$\frac{\partial r}{\partial \rho} = -\frac{M}{V\rho^2} \quad (4.92)$$

It will be convenient to use relative errors rather than absolute errors at this time. If both sides of eq (4.89) are divided by the mixing ratio r , then

$$\frac{s(r)}{r} = \left[\frac{s^2(M)}{M^2} + \frac{s^2(V)}{V^2} + \frac{s^2(\rho)}{\rho^2} \right]^{1/2} \quad (4.93)$$

The nominal value of M is dependent on the duration of a test run, the flow rate of the test gas, and the moisture content of the test gas, whereas $s(M)$ is essentially independent of these parameters. If the test gas has a high moisture content, then at the design flow rates of this apparatus, in a relatively short time enough moisture can be collected in the drying train so that the relative error $s(M)/M$ is reasonably small. However, as the moisture content of the test gas decreases, to collect the same mass of water the duration of a run must be increased. At a given flow rate a low enough moisture content will eventually be reached for which the duration of a run will be inordinately long to maintain the same relative error. Thus for moisture contents below this value, and even for somewhat higher values, the duration of the run will be the factor limiting the accuracy.

It has been estimated that M can be determined with a standard deviation of $13 \times 10^{-5} \text{ g}$ (sec. 4.2.j) provided all the moisture is removed by the first two U-tubes in the main drying train. Assuming that 0.6 g of water are collected, the relative error is thus $13 \times 10^{-5}/0.6$ or 2.2 parts in 10^4 .

The volume of the test gas will be the sum of the number of times each cylinder is filled multiplied by its calibrated volume. The error is the same for each cylinder, so that the total error is the number of fillings times the error for a single filling. Hence the relative error in the total dry air volume is

$$\frac{s(V)}{V} \quad (4.94)$$

irrespective of the number of times a cylinder is filled.

As indicated in sec. 4.3.e, the error is a function of temperature. At 25 °C, the experimental standard deviations of the mean volumes were 2.15 cm³ and 0.99 cm³ for cylinders 1 and 2 whereas the computed value was 0.60 cm³. The value 2.15 cm³, being the largest of the three, will be used as the estimate of the standard deviation for the cylinder volume.

Consider now eq (4.80) where the experimental standard deviation of the mean volume is used instead of the calculated standard deviation of a single volume determination. The equation becomes

$$s(V) = \left[(2.15)^2 + 0.0004 (t - 25^\circ)^2 \right]^{1/2} \quad (4.95)$$

$$= \left[4.62 + 0.0004 (t - 25)^2 \right]^{1/2}$$

The maximum value of $t - 25$ is 10 °C for the instrument. Then $s(V)$ can be shown to be 2.16 cm³. The relative error is $2.16/29.7 \times 10^3$ or 0.73 parts in 10^4 . Since the volume error is almost independent of the bath temperature, the value 0.73 parts in 10^4 will be used for further calculation.

The nominal value of ρ is 1.1×10^{-3} g/cm³. The estimated $s(\rho)$ is 0.14×10^{-6} g/cm³. The relative uncertainty in ρ , i.e., $s(\rho)/\rho$, is therefore 1.3 parts in 10^4 .

The relative standard deviation of the mixing ratio is given by

$$s(r) = \left[(1.3)^2 + (0.73)^2 + (2.2)^2 \right]^{1/2}, \text{ in units per } 10^4,$$

where $1.3/10^4 = s(\rho)$; $0.73/10^4 = s(V)$; $2.2/10^4 = s(m)$, the latter based on collecting 0.6 g of water. Thus $s(r) = 2.7$ parts per 10^4 .

b. Systematic Errors in the Mixing Ratio

In addition to the systematic errors which arise in the measurements of water vapor mass, cylinder volume, and dry air density, there are three other known nonnegligible systematic error sources associated with the operation of the gravimetric hygrometer. These are the incompleteness of water vapor absorption by the U-tubes, an irregular sampling flow rate coupled with a possibility of variation in the test gas moisture content, and leakage of room air into the drying train and cylinders.

Only the extremes of these errors can be estimated, although the actual error in any test could lie anywhere between zero and the extremes. Accordingly, no attempt is made to correct for these errors.

The error arising from two systematic maximum errors of the same sign is given by the algebraic sum of the two. On the other hand, systematic maximum errors of opposite signs may not be added algebraically. Rather, systematic errors of opposite signs give rise to an error band. The upper and

lower error limits are not necessarily the same.

Systematic Errors in Mass of Water Vapor, Cylinder Volume, and Dry Gas Density.—It was shown in secs. 4.2.i, 4.3.f, and 4.4.e that the maximum possible systematic errors in the mass of water vapor, cylinder volume and gas density are respectively ± 0.048 mg, ± 0.48 cm³, and $\pm 0.12 \times 10^{-6}$ g/cm³.

Since the nominal values of these parameters are $m = 0.6$ g, $V = 29.7$ liter, and $\rho = 1.06 \times 10^{-3}$ g/cm³, the relative systematic errors, in units of parts/ 10^4 , are ± 0.80 , ± 0.16 , and ± 1.13 (for m , V , and ρ).

Therefore, these sources contribute a maximum systematic error in the mixing ratio of ± 2.09 parts/ 10^4 .

Incompleteness of Absorption by the U-tubes.—Although the data analysis of the water pick up experiments (sec. 4.2.j) revealed no systematic tendencies, it was suggested in sec. 4.2.g that a maximum of 0.5×10^{-4} mg of water vapor may go undetected for each liter of dry air collected.

The maximum duration of the water pickup runs was nominally 8 hr at a flow of about 1.5 lpm. Thus 720 liters of air were drawn through the absorption tubes and the mass of water vapor that may have escaped absorption was at most $0.5 \times 10^{-4} \times 720$ or 0.04 mg. If in any run the amount was less, it could easily have gone undetected.

Therefore, the experiment described in sec. 4.2.j is not a conclusive basis for assuming the non-existence of this type of systematic error, especially for tests which are more than 8 hr long, and such an error will be assumed to be present.

The nominal air density encountered during tests with the gravimetric hygrometer is 1.06 g/liter. Since the maximum amount of water that may be in the effluent from the absorption tubes is 0.5×10^{-4} mg per liter of air, the measured mixing ratio can be lower than the actual mixing ratio by at most 0.5×10^{-4} mg/1.06 g or 0.47×10^{-4} mg/g, regardless of the magnitude of the mixing ratio.

One of the criteria for the operation of the gravimetric hygrometer is that at least 0.6 g of water vapor shall be collected in any test. Thus a test made at a low moisture content will require a larger volume of test gas to be drawn through the U-tubes and therefore more cylinders to be filled than at a high moisture content. Assuming that the mass of air in a filled cylinder is 31.6 g and that 0.6 g of water vapor is collected per run, a nominal mixing ratio may be computed for a run in which a given number of cylinders are filled.

Table 17 lists examples of the number of cylinder fillings at which a run may be terminated, nominal mixing ratios in units of milligrams of water vapor per gram of associated dry air, and the relative error, E , of the mixing ratio in parts per 10^4 , based on the relation

$$\frac{0.47 \times 10^{-4}}{r} = \frac{E}{10^4} \quad (4.96)$$

where r is the mixing ratio in mg/g.

TABLE 17. *Relative systematic error in mixing ratio from incomplete water absorption^a*

Number of cylinders	Nominal mixing ratio, mg/g	Relative error, parts/10 ⁴
0.7	27.1	-0.017
1	18.9	-0.025
10	1.89	-0.25
40	0.475	-0.99
100	0.189	-2.5

^aMass water vapor = 600 mg, regardless of duration. Mass dry air per cylinder = 31.6 g.

The unabsorbed moisture passes into the cylinders where it is measured as dry air. Therefore the apparent measured amount of dry gas is too high by the amount of vapor present, and this again causes the measured mixing ratio to be smaller than it should be.

Since the molecular weight ratio of water to air is 0.62197, each unit mass of water vapor displaces 1/0.62197 or 1.608 units of air mass. Thus the 0.5×10^{-7} g of water vapor per liter of dry air that flows into the cylinder causes an over statement of the amount of dry air present by 0.8×10^{-7} g for each liter present.

The relative error X in the mass of dry gas is found from the relation

$$\frac{0.8 \times 10^{-7}}{\rho} = \frac{X}{10^4} \quad (4.97)$$

where ρ is the nominal air density which for this calculation may be considered equal to 1 g/liter. The relative error is thus 0.8×10^{-3} parts in 10^4 , which is completely negligible.

Flow Effect Error.—At average sampling flow rates between 1 lpm and the maximum of 2 lpm, the rate is faster when a cylinder begins to fill than when it is almost full. This cyclic sampling affects neither the flow through, nor the output of, the humidity generator, which serves as the source of test gas. However, if the output of moisture content from the generator were to be cyclic during brief time periods, then the possibility arises that the sampling rate and generator output could be synchronous for such periods. Unless the total length of the run were long compared to the synchronous period, a significant systematic error in the average value of the mixing ratio as determined by the gravimetric hygrometer could result.

For example, if the hygrometer were to sample low moisture content air at 2 lpm for 10 min, then high moisture content air at 1 lpm for 10 min, it would sample 20 liters of low moisture content and only 10 liters of high moisture content, biasing the result in favor of the low moisture content.

Because the probability of synchronization is small, the averaging nature of the operation is considered to make this flow effect error negligible for runs in which the number of cylinders filled is greater than three.

For runs in which the number of cylinders filled is less than three, the effect may be eliminated by maintaining the flow at 1 lpm or less. At these lower rates the flow can be maintained with adequate constancy. Since this is the manner in which short runs are performed, the flow effect is negligible over the entire operational range of the instrument.

Subsequent error analysis is based on a flow rate of 1 lpm, so no additional error is introduced by the flow restriction for runs in which the number of cylinders filled is less than three.

Leakage Error.—A leakage check of both cylinders indicates a completely negligible leakage rate at pressures near 20 μ , Hg.

When a check is made on a system consisting of one cylinder and the pressure switch, the leakage rate decreases monotonically from 0.03 cm³/min in a pressure range of 20–50 μ Hg to 0.02 cm³/min in a pressure range of 100–120 μ Hg.

At a sample gas flow rate of 1 lpm, a constant leakage rate of 0.02 cm³/min would contribute an extra 0.02 cm³ of room air to every liter of dry test gas, an error of two parts in 10^5 in the volume of the dried test gas. However, since the leakage rate probably decreases below 0.02 cm³/min as the pressure increases, the error it contributes to the air volume in the cylinders is considered to be negligible.

The main drying train was subjected to separate leakage tests. Air leaking into the train enters from the room, carrying water vapor that is absorbed in the U-tubes. The tests indicate approximate leakages of 0.003 cm³/min at pressures in the micron Hg range, and 0.002 cm³/min at a nominal pressure of 340 mm Hg. This leakage apparently does not decrease appreciably with increasing pressure, and it will be assumed that the leakage rate of 0.002 cm³/min holds over the entire range of pressures. Furthermore, it will be assumed that the entire leakage occurs into the first two tubes of the main drying train, where the water vapor in the incoming room air is picked up and later weighed as part of the total water mass. The dried air from the leakage then passes on into the cylinders, where it is measured as part of the total dry air mass.

The mixing ratio is given by eq (1.1). However, since there is leakage, the mixing ratio actually measured is given by

$$r = (M + \rho_{wa}V') / (V\rho + V'\rho') \quad (4.98)$$

where M , V and ρ are the quantities defined for eq (1.1), and

ρ_{wa} = mass of water vapor per unit volume of dry room air, g/liter

ρ' = density of dry room air, g/liter

V' = volume of dry room air entering the system, liter.

The mass of dry air collected per cylinder, $V\rho$, is

about 31.6 g, and the mass of water collected per run, M , is about 0.6 g.

If a flow rate of 1 lpm is assumed, then it takes 30 min to fill a cylinder, and the total volume of room air leaking into the drying train during the filling of each cylinder is 6×10^{-5} liters. Assuming the nominal room air density to be 1.17 g/liter, the mass of dry air, per cylinder, from the leakage into the absorption tubes is $1.17 \times 6 \times 10^{-5}$ g or 7.02×10^{-5} g.

To assess the quantity $\rho_{w_a} V'$, the water vapor mass from the room air that is collected in the U-tubes, it is necessary to consider conditions of both maximum and minimum water vapor density in the ambient air in the vicinity of the drying train.

The lowest temperature in the area in which the hygrometer is used may be about 19 °C. A room relative humidity of 10 percent is assumed possible at this temperature. At this temperature the saturation concentration of water vapor in air is 16.31×10^{-3} g water vapor/liter of air, so that at a relative humidity of 10 percent, the concentration is 1.631×10^{-3} g water vapor/liter of air. Since 6×10^{-5} liters of room air leak into the system per cylinder, $1.631 \times 6 \times 10^{-8}$ or 9.8×10^{-8} g of water vapor are collected from the leakage for each cylinder filling.

The highest ambient temperature is 28 °C, with a possible relative humidity of 60 percent. The saturation concentration is 27.24×10^{-3} g water vapor/liter of air, so that at a relative humidity of

60 percent the concentration is 16.344×10^{-3} g water vapor/liter of air. Thus $6 \times 10^{-5} \times 16.344 \times 10^{-3}$ or 98.1×10^{-8} g of water vapor is collected from the leakage, for each cylinder.

In table 18 are tabulated the masses of air and water gained from both the test gas and the leakage gas under the conditions of maximum and minimum observed water vapor density in the ambient air, for tests involving different numbers of cylinder fillings.

Table 19 is a continuation of table 18, in which the "true" mixing ratio (based on the assumptions of collecting 0.6 g water vapor per run and that the mass of associated dry air per cylinder is 31.6 g), and the measured mixing ratio (assuming leakage in addition to the above) are given, along with the relative systematic error.

The mixing ratios have been computed to as many figures as was necessary to get an error indication.

When the room-air mixing ratio is less than the test-gas mixing ratio, the error sign is negative, and for the inverse situation, the error sign is positive.

c. Overall Error in Mixing Ratio

The discussion of sec. 4.5.b was based on estimates of the maximum contributions to the systematic uncertainty in a mixing ratio determination expected from various parameters.

TABLE 18.—*Water vapor and air masses collected from leakage and the test gas*

No. of cyl.	Room temp. and RH	A	B	C	D
		Water gained from leak (mg)	Water gained from test gas (mg)	Air gained from leak (g)	Air gained from test gas (g)
0.7	19 °C 10% RH	6.9×10^{-5}	600	4.91×10^{-5}	22.1
1		9.8×10^{-5}	600	7.02×10^{-5}	31.6
10		98×10^{-5}	600	70.2×10^{-5}	316
40		392×10^{-5}	600	280×10^{-5}	1264
100		980×10^{-5}	600	702×10^{-5}	3160
0.7	28 °C 60% RH	69×10^{-5}	600	4.91×10^{-5}	22.1
1		98×10^{-5}	600	7.02×10^{-5}	31.6
10		980×10^{-5}	600	70.2×10^{-5}	316
40		0.039	600	280×10^{-5}	1264
100		0.098	600	702×10^{-5}	3160

TABLE 19.—*Relative systematic error in mixing ratio from leakage, for runs of various lengths*

No. of cyl.	Room temp. and RH	E	F	Error, parts per 10^4 $\frac{F-E}{E} \times 10^4$
		"True" mixing ratio, mg/g ^a	Observed mixing ratio, mg/g ^b	
0.7	19 °C 10% RH	27.14932	27.14926	-0.02
1		18.98734	18.98730	-0.02
10		1.898734	1.898733	-0.01
40		0.4746835	0.4746856	+0.04
100		0.1898734	0.1898761	+0.14
0.7	28 °C 60% RH	27.14932	27.14929	-0.01
1		18.98734	18.98733	+0.01
10		1.898734	1.898761	+0.14
40		0.4746835	0.4747133	+0.63
100		0.1898734	0.1899040	+1.61

^a Column B/D, table 18. ^b Columns (A + B)/(C + D), table 18.

TABLE 20.—Summary of maximum errors, parts per 10⁴

Random			Systematic		
No. of cyl.	Nominal mixing ratio, mg/g	3 × SD	Errors in <i>M</i> , <i>ρ</i> , <i>V</i>	Incomplete water absorption	Leakage
0.7	27.1	± 8.1	± 2.09	− 0.017	− 0.02
1	18.9	± 8.1	± 2.09	− 0.025	− 0.02
10	1.89	± 8.1	± 2.09	− 0.25	+ 0.14, − 0.01
40	0.475	± 8.1	± 2.09	− 0.99	+ 0.63
100	0.189	± 8.1	± 2.09	− 2.5	+ 1.61

It was shown in sec. 4.5.a that random errors gave rise to a relative standard deviation of the mixing ratio of 2.7 parts in 10⁴. The maximum contribution of the random errors to the uncertainty in a mixing ratio determination is considered to be three standard deviations or ± 8.1 parts in 10⁴.

Examples of runs in which a given number of cylinders are filled are listed in table 20, along with the corresponding nominal mixing ratios, and the maximum relative errors and their sources.

For any run, the maximum negative and positive limits of error may be determined by summing separately the negative errors and the positive errors. Consider a run in which only 0.7 of a cylinder is filled, as an example. The negative errors listed in table 20 are, in units of parts per 10⁴, − 8.1, − 2.09, − 0.017, and − 0.02, the sum of which is nominally − 10.2. This defines the lower error limit in this case. The positive errors are 8.1 and 2.09, the sum

of which is nominally + 10.2. This defines the upper error limit.

Therefore, for a run in which only 0.7 of a cylinder is filled, the error in mixing ratio will lie in the band from − 10.2 to + 10.2 parts in 10⁴. Similar calculations may be made for runs involving any number of cylinder fillings. A synopsis of such calculations is presented below.

No. of cylinders	Mixing ratio, mg/g	Error band, parts/10 ⁴
0.7	27.1	− 10.2 to + 10.2
1	18.9	− 10.2 to + 10.2
10	1.89	− 10.4 to + 10.3
40	0.475	− 11.2 to + 10.8
100	0.189	− 12.7 to + 11.8

5. Conclusions and Discussions

The National Bureau of Standards has developed a hygrometer for the measurement of mixing ratios lying in the range from 27 mg/g to 0.19 mg/g.

The highest measurable value is determined by consideration of operator comfort. An ambient room temperature slightly above 30 °C is tolerable for short periods, and to prevent condensation in the lines, the room temperature must be above the dewpoint temperature. This limits the upper dewpoint of the test gas to 30 °C, corresponding to a mixing ratio of nominally 27 mg/g, although the hygrometer itself is capable of measuring a higher value.

The lower limit, 0.19 mg/g, is determined pri-

marily by error considerations, since it is seen that systematic errors from leakage and incomplete absorption become important in this range.

The estimated maximum error magnitude encountered over the operational range of the instrument is 12.7 parts in 10⁴, or 0.13 percent of the measured value.

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7. Appendix—Details of the Operation of the Automatic Control Circuit (Refer to figures 2, 4, and 6)

Assume that cylinder no. 1 has been evacuated and that cylinder no. 2 is being filled with test gas. The pressure switch senses the increasing pressure in cylinder no. 2. When this pressure reaches 700 mm Hg, valve *g* closes and valve *G* opens. The pressure switch is now in communication with cylinder no. 1, so that the mercury in the pressure switch immediately drops, successively exposing each of the five photocells to light from its respective lamp. Upon illumination, each photocell, through a

vacuum tube amplifier, energizes an associated relay.

Relay *K1* is a SPDT plate relay with contacts so connected to 110 volts d-c and coil *A* of Relay *K2* that this coil is energized only when relays *K1*, *K2B*, and *K5* are unenergized. Relay *K2* is a 4PDT mechanical latching relay with two independent coils. An impulse of power to coil *K2A* mechanically latches all contacts in position *A*; an impulse of power to coil *K2B* mechanically latches all contacts

in position *B*. As the mercury in the pressure switch reaches 700 mm, *K1* is deenergized, *K2A* is energized and 110 volts a-c is applied to relays *K3* and *K4*. Relays *K3* and *K4* are 4PDT impulse relays whose contacts alternate between positions *A* and *B* with successive applications of power to their coils. The contacts of relay *K4* are wired so that power is applied to either of two solenoid valves *L5* or *L6*. These solenoid valves, through air piston actuators, *A5* and *A6*, open and close valves *G* and *g*. Relay *K4* is phased to close valve *g* and open valve *G* when the pressure in cylinder no. 2 increases to 700 mm Hg. The contacts of relay *K3* are wired to control valves *H*, *I*, *h*, and *i*. Poles *V-V* and *U-U* of relay *K3* are mechanically linked so that when poles *V-V* are in position *A*, Poles *U-U* are in position *B* and vice versa. Further, poles *V-V* have to be in position *A* before the solenoid valve *L1* can be energized to open valve *i* and in position *B* for *L2* to open valve *I*. Similarly, poles *U-U* have to be in position *B* for *L4* to open valve *h* and in position *A* for *L3* to open valve *H*. Relay *K3* is phased so that poles *V-V* close in position *A* and poles *U-U* close in position *B* when the pressure in cylinder no. 2 increases to 700 mm Hg. The application of power to solenoid valves *L1*, *L2*, *L3*, and *L4* depends not only on relay *K3* but also on relays *K5*, *K6*, *K7*, and *K8*.

As soon as valve *G* opens and *g* closes, the mercury in the pressure switch drops. As the mercury falls below 700 mm, relay *K1* is energized and *K2A* is deenergized. However, the contacts of relays *K2*, *K3*, and *K4* remain latched in their previous positions. When the mercury in the pressure switch reaches 690 mm, relay *K5* is energized, when it reaches 410 mm, relay *K6* is energized, when it reaches 400 mm, relay *K7* is energized, and when it reaches 50 mm, relay *K8* is energized. Relay *K8* is a 6PDT telephone relay, one contact, *M*, of which is connected to a contact, *M*, on *K5* and then to a 1.5 volt battery. As long as relay *K5* is energized, a biasing voltage of 1.5 volts is applied to one grid of tube *V3*, maintaining continuous current flow through relay *K8*, and then from plate to cathode of *V3*, thereby keeping *K8* energized irrespective of whether its photocell is illuminated or not, and holding all poles of *K8* in position *A*.

With relays *K1*, *K5*, *K6*, *K7*, and *K8* energized, 110 volts d-c is applied, through poles *U-U*, to one or the other of the solenoid valves controlling cylinder valves *H* and *h*. Since the Poles *U-U* of *K3* are in position *B* when the pressure switch is in communication with cylinder no. 1 (as described above), the energizing of *K8* applies power to the solenoid valve *L4* controlling cylinder valve *h*, thereby opening valve *h* while valve *H* remains closed. Valve *h* remains open until the pressure in cylinder no. 1 rises to 400 mm Hg, at which pressure relay *K7* is deenergized.

When the pressure in cylinder no. 1 increases to 410 mm Hg, relay *K6* deenergizes, and 110 volts d-c

is applied through poles *V-V* to either solenoid valves *L2* or *L1* controlling valves *I* and *i*. The phasing of relay *K3* is such (when the pressure switch is open to cylinder no. 1) that poles *V-V* are in position *A*. Valve *i* opens at 410 mm Hg, and then closes when the pressure reaches 690 mm Hg, that is when relay *K5* deenergizes.

Relay *K8* is also used to reverse the poles of relay *K2* from position *A* to *B*, for up to this time relay *K2* has remained latched in position *A*. This is accomplished by applying 110 volts d-c, through poles *W-W* to coil *K2B*. Although relay *K8* opens when the pressure switch reaches 690 mm, and power is removed from coil *K2B*, the poles of relay *K2* stay latched in position *B*. At 700 mm Hg, relay *K1* is deenergized, leading to the energizing of coil *K2A*, the closing of relay *K2* in position *A*, and the energizing of relays *K3* and *K4*.

Relay *K8* opens when the pressure reaches 690 mm Hg, for then relay *K5* is deenergized and the biasing voltage is removed from the grid of *V3*.

When the pressure in cylinder no. 1 reaches 700 mm Hg, relay *K1* is deenergized. In a manner analogous to that already described, the poles of relays *K3* and *K4* reverse their positions, cylinder valve *G* closes and *g* opens, and the entire procedure is repeated. This time the pressure switch senses the pressure in cylinder no. 2.

When vacuum exhaust valve *I* or *i* is opened, gas at a pressure of 700 mm Hg is trapped and sealed in the space between the valve body, the exterior of the ball, and the annular seats at entrance and exit. When the valve is closed this trapped volume of gas is discharged, in part, into its adjoining evacuated cylinder, thereby producing a slight rise in pressure in the cylinder. To rectify this, a scheme is employed that automatically triggers the exhaust valve once during the evacuation process, that is, momentarily closes and then reopens the valve. Relay *K9* is a DPDT ratchet relay, of which one pole is used. With each pulse of energy to the coil of this relay, the pole is reversed from one contact position to the other, and remains locked in this position until the next pulse. The coil of relay *K9* is connected, in parallel, with contacts *V-V* of relay *K8*. Thus, whenever voltage appears at contacts *V-V*, voltage is applied to the coil of relay *K9*. Assume that the pole of *K9* is initially in position *B*. It now moves to position *A*, and 110 v a-c is fed to a small synchronous timing motor. The latter, through suitable gears and a cam, operates a microswitch. The switch is connected between contacts of relays *K5* and *K6*, and is part of the circuit that feeds voltage to contacts *V-V* of relay *K8*. The break in this circuit removes the impressed voltage from the coil of relay *K9*. However, because its contacts are locked in position and will remain so until voltage is again applied to its coil, the timing motor and cam continue to rotate. The microswitch contacts are closed and once again, the coil of relay *K9* is energized. This time the pole of *K9* moves to position *B*, the timing motor stops, and the microswitch

contacts remain closed. The net effect of this sequence of operations has been to interrupt, momentarily the flow of current to contacts *V-V* and, consequently, to close and reopen the appropriate vacuum exhaust valve. This sequence of operations is repeated once during each cycle of evacuation and filling for each cylinder.

The pole on relay *K9* is arranged to be in position *B* just prior to the start of an evacuation. The cam position is adjusted so that the microswitch is in the just closed position. Therefore at the initiation of an evacuation the cam must make one revolution before it breaks open the contacts on the microswitch. This takes 2 min, allowing ample time for the cylinder to have been evacuated to a residual pressure of less than 50 microns.

A neon lamp, in series with a resistor, is connected in parallel with the solenoid of each solenoid valve and serves as a pilot light to indicate whenever a cylinder valve is open. In addition, there is a switch in each solenoid circuit which permits each cylinder valve to be opened or closed at will. Switches *S1*, *S2*, *S3*, *S4*, *S5*, and *S6* are DPDT center-off toggle switches. In the center-off position, each solenoid valve is deenergized and each cylinder valve is therefore closed. In the *A* position, each solenoid valve is controlled by the automatic sequencing operations of the pressure switch. In the *B* position, power is applied to the solenoid and the corresponding cylinder valve opens.

Cylinder valves *J* and *j* are manually controlled through DPDT center-off toggle switch *S7*. Both valves are closed when *S7* is in the center-off position; valve *J* opens when *S7* is in position *A* while valve *j* opens when *S7* is in position *B*.

The power for the photocell-amplifier-relay circuits is supplied by the power pack shown in figure 6.

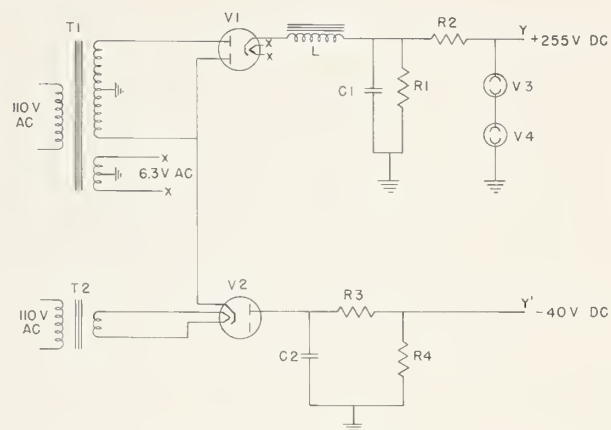


FIGURE 6. Power supply for valve sequencing and control circuit. *T*₁, power transformer; *T*₂, filament transformer; *L*, filter choke; 10 H; *C*₁, 20 μfd; *R*₁, 27 K, 1 W; *R*₂, 1 K, 10 W; *R*₃, 100 k, $\frac{1}{2}$ W; *R*₄, 10 k, $\frac{1}{2}$ W; *V*₁ and *V*₂, 6X4; *V*₃, VR OC3; *V*₄, VR OD3.



